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Environmental Assessment Data Base for High-Btu Gasification Technology
Volume III. Appendices D, E, and F

TRW Environmental Engineering Div, Redondo Beach, CA

Prepared for

Industrial Environmental Research Lab, Research Triangle Park, NC

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Research Triangle Park NC 27711

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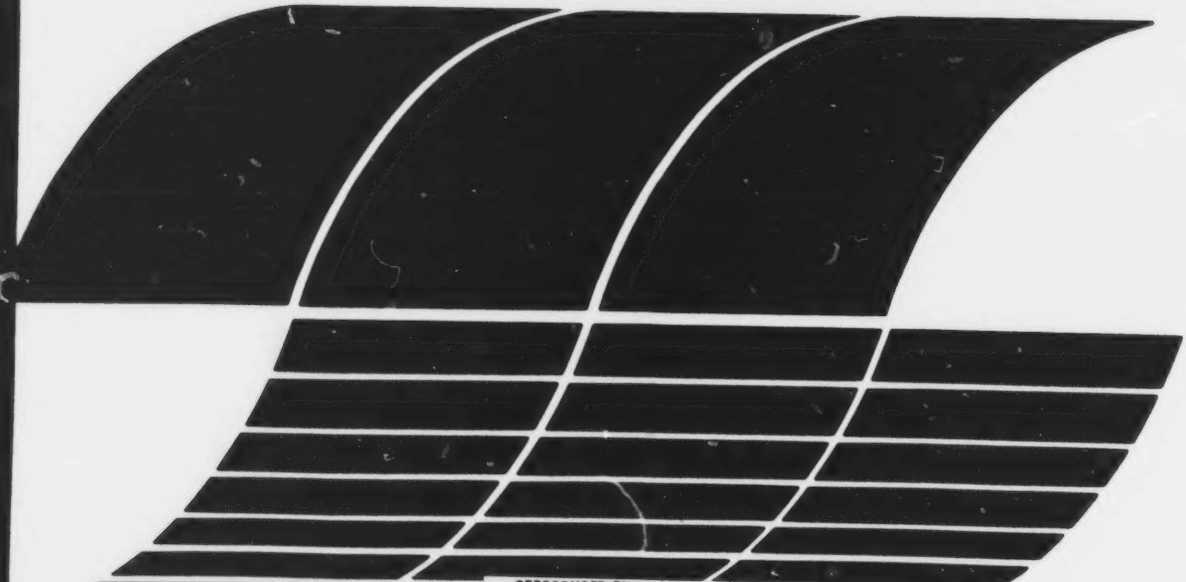
Interagency Energy/Environment R&D Program Report



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16. ABSTRACT

The report is part of a comprehensive EPA program for the environmental assessment (EA) of high-Btu gasification technology. It summarizes and analyzes the existing data base for the EA of technology and identifies limitations of available data. Results of the data base analysis indicate that there currently are insufficient data for comprehensive EA. The data are limited since: (1) there are no integrated plants, (2) some of the pilot plant data are not applicable to commercial operations, (3) available pilot plant data are generally not very comprehensive in that not all streams and constitutents/parameters of environmental interest are addressed, (4) there is a lack of experience with control processes/equipment in high-Btu gasification service, and (5) toxicological and ecological implications of constituents in high-Btu gasification waste streams are not established. A number of programs are currently under way or planned which should generate some of the needed data. The report consists of three volumes: Volume I summarizes and analyzes the data base; Volume II contains data sheets on gasification, gas purification, and gas upgrading; and Volume III contains data sheets on air and water pollution control and on solid waste management.

17. KEY WORDS AND DOCUMENT ANALYSIS

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M. Ghassemi, K. Crawford, and S. Quinlivan

TRW Environmental Engineering Division
One Space Park
Redondo Beach, California 90278

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APPENDIX D

AIR POLLUTION CONTROL

Hydrogen Sulfide Control Module

Claus

Stretford (see Acid Gas Removal Module, Appendix B)

Giammarco-Vetrocoke (see Acid Gas Removal Module, Appendix B)

CLAUS PROCESS

1.0 General Information

1.1 Operating Principles - The catalytic oxidation of H_2S, in an acid gas stream, to elemental sulfur and the recovery of the sulfur. The catalyst used is either bauxite or alumina in the form of pellets or balls.

1.2 Development Status - Commercially available.

1.3 Licensor/Developer - The Ralph M. Parsons Co.
100 W. Walnut Street
Pasadena, CA 91124

1.4 Commercial Applications(1) - There are approximately 170 Claus plants in the United States used in a wide variety of industries including natural gas and coke production(1).* One application of the Claus process to coal conversion gas purification is in South Africa(12).

2.0 Process Information(2,12)

2.1 Flow Diagram - There are three basic forms of the Claus Process: "split-stream," "straight-through," and the "sulfur burning" mode. The "split-stream" process is used when the CO_2 concentration exceeds 30% (volume); the "straight-through" process is generally used when the feed gas stream contains less than 30% (volume) CO_2. The "sulfur burning" mode is employed where low H_2S levels (5%-10%) are to be treated.

In most coal conversion processes the acid gas stream produced as a result of acid gas treatment will contain CO_2 in excess of 30%

---

*For specific information on plant locations, sulfur production, companies operating Claus plants and companies which design Claus plants, see Reference 1.

(volume); therefore, the "split-stream" Claus process would be applicable.* In the "split-stream" process (Figure D-1) the acid gas, Stream 1, enters the system through a knockout vessel (where entrained liquids are removed) and is then split into two streams (4 and 5). Stream 5 enters a sulfur burner where the H_2S is oxidized to SO_2 using a stoichiometric quantity of air. Hot gases enter a reaction furnace; enough residence time is provided for the Claus reaction to reach equilibrium. The gas is then passed through a waste heat boiler and a condenser (where the elemental sulfur produced is removed) and then it is combined with Stream 4. The combined stream is then reheated and sent to the first catalytic converter for further Claus reaction. A plant may operate with any number of catalytic converters, depending on the desired sulfur recovery efficienciy.

The "straight-through" system (Figure D-2) is similar to the above system with the following exceptions: upon existing the knock-out drum, the entire volume of gas is sent to a sulfur burner where it is oxidized under free-flame conditions with a stoichiometric quantity of air; it then passes through the reaction furnace, waste heat boiler, first condenser, reheater, and converter.

The "sulfur burning" mode is similar to the "split stream" mode except that liquid sulfur is injected into the combustion chamber to supply SO_2 for the Claus reaction.

2.2 Equipment - Reaction furnace, sulfur condensers, reheaters, catalytic converters, waste heat boilers.

2.3 Feed Stream Requirements - Claus plants can be designed to operate at various temperatures and pressures, and with a wide variation of feed stream compositions.(3)

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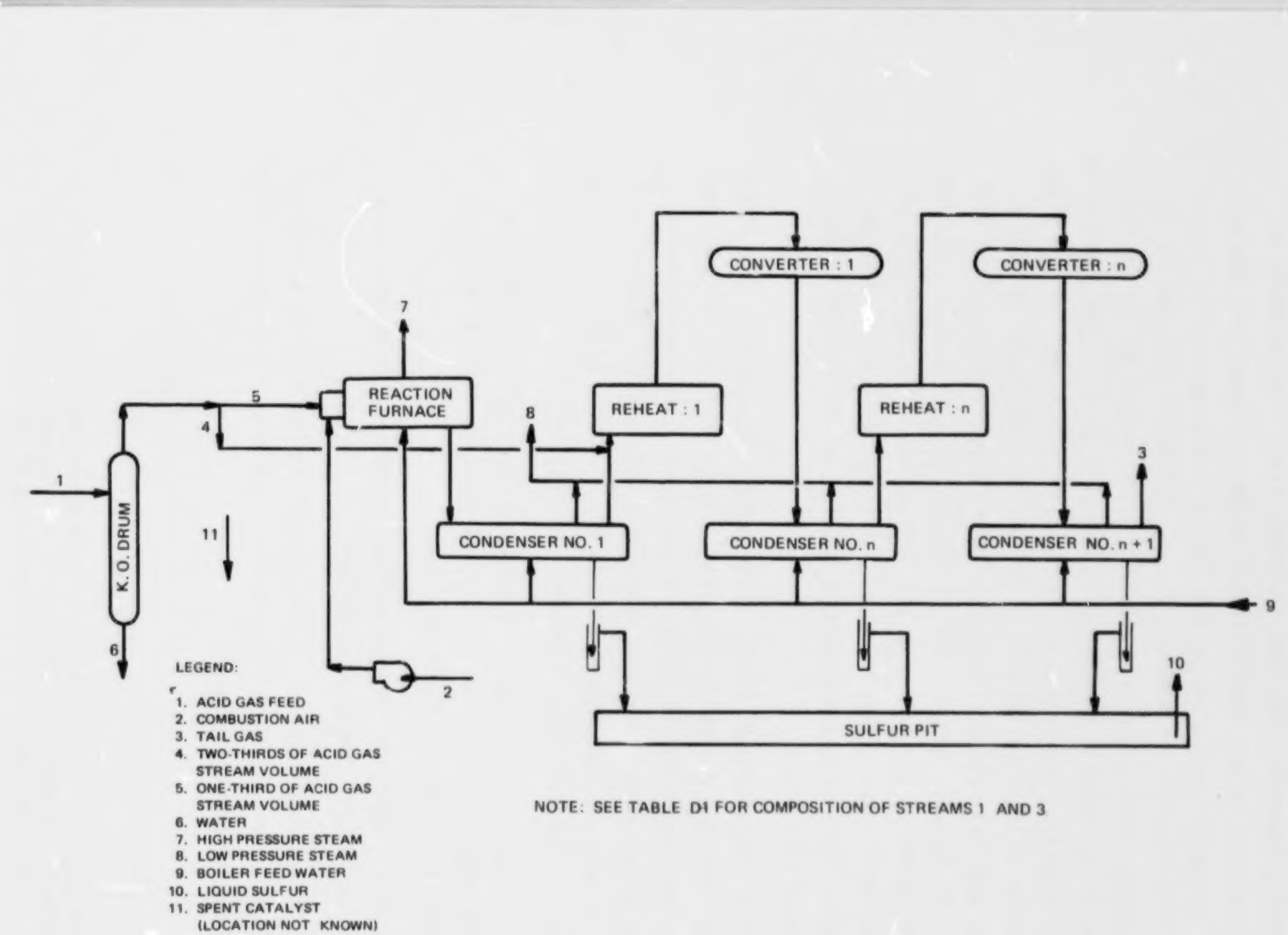
*The 30% maximum CO_2 level for straight-through operation can be extended by the use of preheat. Hydrocarbons in feed also influence straight-through applicability, since they may limit the bypassing of gas directly to the converters.

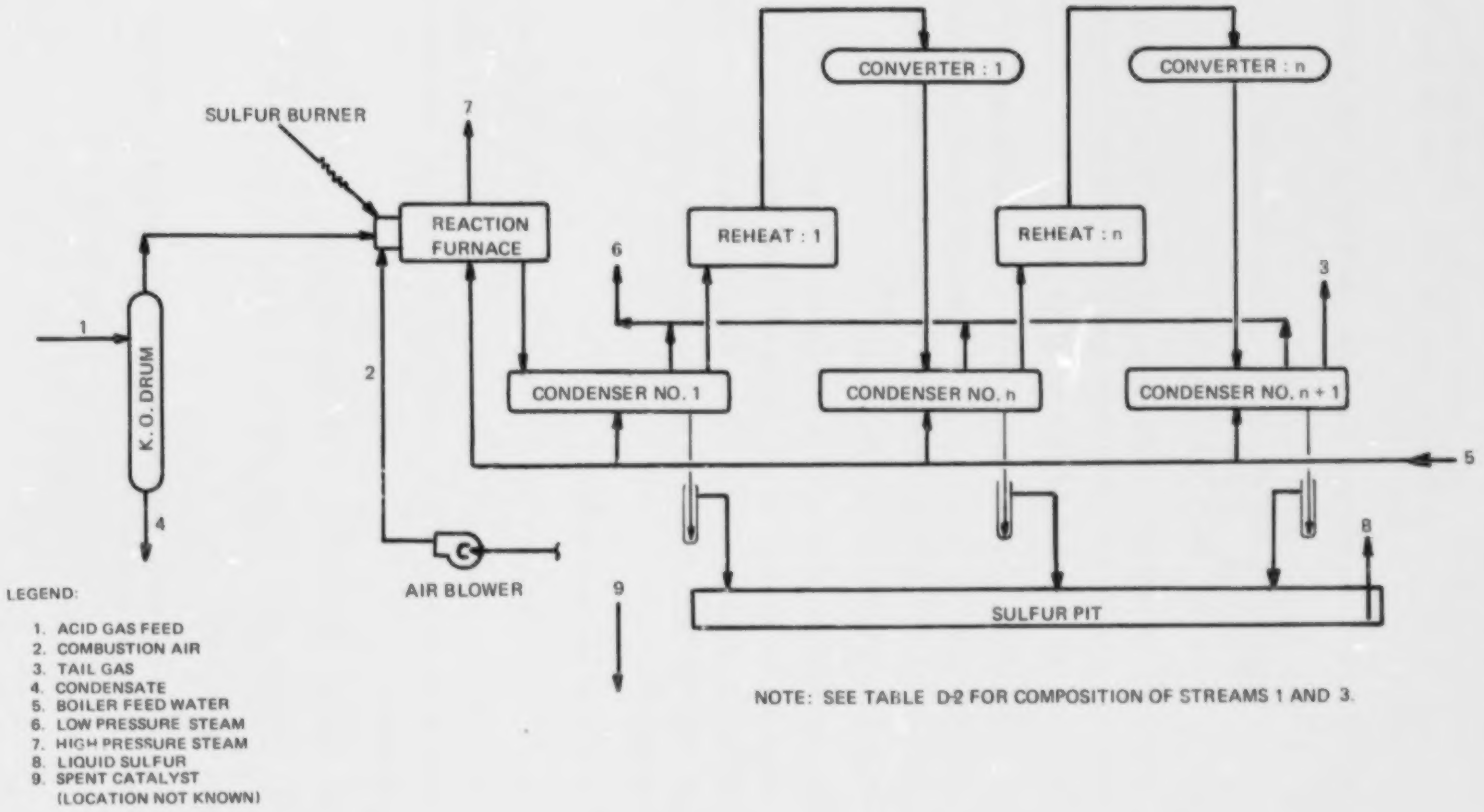

1
K. O. DRUM
6
11
5
4
REACTION FURNACE
7
2
8
REHEAT : 1
CONVERTER : 1
REHEAT : n
CONVERTER : n
3
CONDENSER NO. 1
CONDENSER NO. n
CONDENSER NO. n + 1
9
10
SULFUR PIT

LEGEND:

1. ACID GAS FEED
2. COMBUSTION AIR
3. TAIL GAS
4. TWO-THIRDS OF ACID GAS STREAM VOLUME
5. ONE-THIRD OF ACID GAS STREAM VOLUME
6. WATER
7. HIGH PRESSURE STEAM
8. LOW PRESSURE STEAM
9. BOILER FEED WATER
10. LIQUID SULFUR
11. SPENT CATALYST (LOCATION NOT KNOWN)

NOTE: SEE TABLE D1 FOR COMPOSITION OF STREAMS 1 AND 3

Figure D-1. Split-Stream Claus Process(3)


SULFUR BURNER
REACTION FURNACE
K.O. DRUM
AIR BLOWER
CONDENSER NO. 1
CONDENSER NO. n
CONDENSER NO. n + 1
REHEAT : 1
REHEAT : n
CONVERTER : 1
CONVERTER : n
SULFUR PIT
1
2
3
4
5
6
7
8
9
LEGEND:
1. ACID GAS FEED
2. COMBUSTION AIR
3. TAIL GAS
4. CONDENSATE
5. BOILER FEED WATER
6. LOW PRESSURE STEAM
7. HIGH PRESSURE STEAM
8. LIQUID SULFUR
9. SPENT CATALYST (LOCATION NOT KNOWN)

NOTE: SEE TABLE D-2 FOR COMPOSITION OF STREAMS 1 AND 3.

Figure D-2. Straight-Through Claus Process(3)

- H_2S concentration is the most important parameter in Claus plant design and operation. Gases with H_2S concentrations from less than 10 vol. % to greater than 90 vol. % can be handled by various Claus plant designs(4,12).

- "Standard" conditions have been defined as the following(3):

  - H_2S content 90% by volume
  - Hydrocarbon content 2% by volume as ethane
  - Temperature: 311°K (100°F)
  - Pressure: 0.14 MPa (6 psig)

2.4 Operating Parameters - Operating temperatures will vary as a function of feed stream conditions and plant design. Pressures are usually low (below 0.17 MPa or 25 psia).

2.5 Process Efficiency and Reliability - For operating conditions defined as "standard" in Section 2.3, a "typical" plant (3-stage Claus) is capable of 97% sulfur recovery(3). Efficiency decreases as the catalyst becomes partially deactivated(12).

No information available which would indicate special maintenance problems or unusual hazardous conditions created by the process. Principal problems result from frequent shutdown periods from lack of feed or from upsets caused by operating problems in upstream units(12).

2.6 Raw Material Requirements

- Catalyst makeup: half life is at least two to three years(12).

2.7 Utility Requirements(4) - Utility requirements will vary. For gas stream containing 40% H_2S and 60% CO_2, typical requirements are as follows:

- Boiler feed water: 6.25 l/kg of sulfur (0.75 gal/lb)
- Electricity: 0.088 kwh/kg of sulfur (0.05 kwh/lb)

3.0 Process Advantages

- Commercially proven process for bulk H_2S removal; process is well known and used extensively
- Produces high purity salable sulfur

- Produces steam

- Process design can be readily altered to accommodate a wide range of feed gas conditions(5). Such process modifications may consist of use of a multizone combustion chamber and control of flow rate, temperature and combustion air.

4.0 Process Limitations

- The carryover of high molecular weight hydrocarbons can cause deactivation of the catalyst because such compounds can adsorb on the catalyst and eventually char(6).

- Low molecular weight hydrocarbons in feed can cause increased furnace temperatures and dilution of reactive sulfur compounds which decrease conversion efficiency. Carbon oxides formed by hydrocarbon combustion can increase COS and CS_2 formation in the Claus furnace.

- Catalyst plugging problems can occur when NH_3 concentration exceeds 500 ppmv in combination with CO_2 concentrations greater than 30% (vol)(3). If CO_2 is low in feed gas, higher levels of ammonia can, by design modifications, be handled (up to 18%)(12).

- Excessive hydrocarbons in feed can lead to elevated operating temperatures which can cause accelerated aging of the catalyst(6).

- The presence of HCN in the acid gas can lead to excessive equipment corrosion and catalyst deactivation via formation of thiocyanates(7).

- The presence of various contaminants in the acid gas feed (e.g., NH_3, H_2O, CO_2, hydrocarbons) can lower the sulfur removal ability of the Claus process and increase the size of the plant required due to larger volumetric flow rates(8).

- COS and CS_2, if present in the feed, are not usually converted to H_2S and then to elemental sulfur in Claus plants using standard catalysts. Some COS and CS_2 are actually formed in Claus plants when feeds high in CO and CO_2 are processed.

5.0 Process Economics(1)

- The cost of a Claus plant varies as a function of two major parameters: the percent of H_2S in the acid gas feed; and the daily capacity of sulfur production.*

---

*If ammonia containing acid gas is burned, the amount becomes a factor in plant size and cost.

- The approximate costs as estimated in 1973 are as follows:

Mole % H_2S in Acid Gas Feed	Claus Plant Investment (102 tonne/day plant size)	Sulfur Production Cost per Tonne
15	$1,400,000	$14
50	$1,000,000	$11
90	$ 900,000	$ 9

Daily Sulfur Production Capacity (Tonne)	Claus Plant Investment (assumes H_2S concentration in feed at 50%)	Sulfur Production Cost per Tonne
10	$ 300,000	$26
102	$1,000,000	$11
1020	$4,300,000	$ 8

6.0 Input Streams (see Figure 1)

- Acid gas stream: (Stream 1); see Tables D-1 and D-2

7.0 Discharge Streams (see Figure D-1)

- Tail-Gas: (Stream 3); see Tables D-1 and D-2
- Condensate (Stream 6): no data available
- Spent Catalyst (Stream 11): no composition/properties data available; see Section 2.6 for makeup requirements.

8.0 Data Gaps and Limitations

- Process applicability to coal conversion process gas purification systems not entirely established.
- Definition of the maximum allowable concentrations of various contaminants in the feed gas; e.g., NH_3, COS, CS_2, trace metals, HCN, carbonaceous matter.
- The effects that various contaminants (trace metals, carbonaceous matter, etc.) have on the process and the ultimate fate of such contaminants in the system.

9.0 Related Programs

A Claus plant is featured in the design of the Hygas pilot plant at Chicago, Illinois for processing the acid gas stream from a DGA unit(13). No data are available on the operation of this Claus plant at present.

TABLE D-1. SPLIT FLOW MODE CLAUS FEED AND TAIL GAS DATA(9)*

Component	Feed Stream Stream 1 Mole %	Tail Gas Stream Stream 3 Mole %
COS	----	0.09
H_2S	19.72	0.26
SO_2	----	0.10
CO_2	78.68	65.04
N_2	0.56	34.34
C_1	0.66	----
C_2	0.12	0.19
C_3	0.08	0.03
C_4	0.18	----
C_5^+	----	----
Temperature	313°K (105°F)	805°K (990°F)
Pressure	0.16 MPa (8.1 psig)	0.10 MPa (0.1 psig)
Flow (wet basis)	518000 Nm^3/d (19,272 mcf/d)	1,073,000 Nm^3/d (37,920 mcf/d

*Data were selected to represent Claus performance on low H_2S, high CO_2 gases which would be encountered in coal gasification applications.

TABLE D-2. STRAIGHT THROUGH CLAUS FEED AND TAIL GAS DATA(8)

Acid Gas Feed Stream 1		Tail Gas* Stream 3	
Components	Mole %	Composition	Mole %
H_2S	90.1	N_2	62
CO_2	3.6	CO_2	1.4
CH_4	0.8	H_2O	35
C_2H_6	0.4	H_2S	0.30
NH_3	0	SO_2	0.43
H_2O	5.1	$S_6 + S_8$	0.02
		Entrained Liquid S^0	0.13

*Data given are after incineration.

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13. Information provided to TRW by the Institute of Gas Technology, May 1978.

Tail Gas Treatment Module

SCOT

Beavon

IFP

Sulfreen

Cleanair

SCOT (SHELL CLAUS OFF-GAS TREATMENT) PROCESS

1.0 General Information(1,2)

1.1 Operating Principles - The purification of Claus plant tail gas by the catalytic reduction of sulfur species to H_2S followed by the removal and recovery of the H_2S in an alkanolamine scrubbing system. A reducing gas (e.g. hydrogen) is used as the reductant and cobalt/molybdate catalyst is used).

1.2 Development Status - Commercially available.

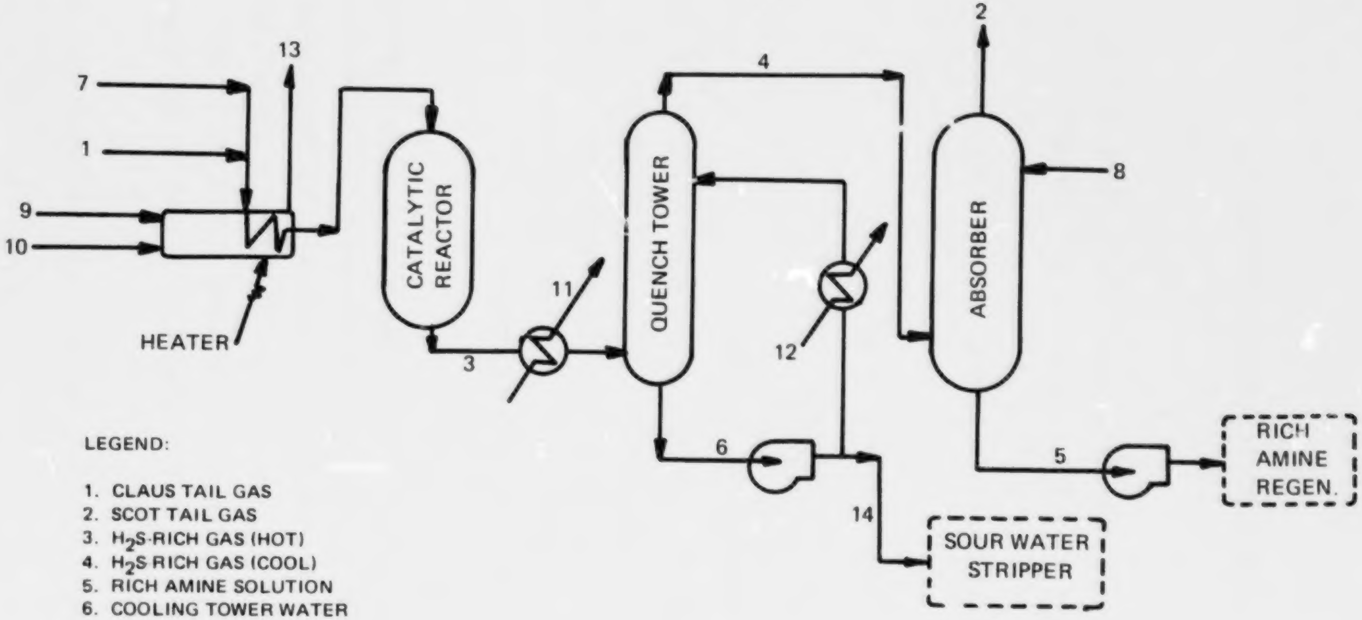
1.3 Licensor/Developer - Shell Development Company
One Shell Plaza
P. O. Box 2463
Houston, Texas 77001

1.4 Commercial Applications(6) - Primary application is for Claus plant tail gas treatment; fourteen plants are licensed and operating (see Figure D-3), and approximately 20 others are in various stages of planning, design, and construction. No known application to coal conversion type processes have been reported.

2.0 Process Information

2.1 Flow Diagram(2,4) (see Figure D-3) - Claus plant tail gas, Stream 1, is heated, then sent to a catalytic reactor where the sulfur species are converted to H_2S. This H_2S stream, Stream 3, is then cooled and sent to an alkanolamine gas treating system typically containing diisopropanolamine. The rich amine solution, Stream 5, is sent to an amine regeneration unit, and cleaned gas is sent to the Claus plant incinerator.

2.2 Equipment - Conventional catalytic reactor, cooler, absorber, and stripper.


13
7
1
9
10
HEATER
CATALYTIC REACTOR
3
11
4
QUENCH TOWER
12
6
14
2
8
ABSORBER
5
RICH AMINE REGEN.
SOUR WATER STRIPPER

LEGEND:

1. CLAUS TAIL GAS
2. SCOT TAIL GAS
3. H_2S-RICH GAS (HOT)
4. H_2S-RICH GAS (COOL)
5. RICH AMINE SOLUTION
6. COOLING TOWER WATER
7. REDUCING GAS (H_2)
8. LEAN AMINE SOLUTION
9. FUEL GAS
10. AIR
11. L. P. STREAM
12. COOLING AIR OR WATER
13. FLUE GAS
14. CONDENSATE

SOUR WATER STRIPPER AND RICH AMINE REGENERATOR ARE SYSTEMS ALREADY EXISTING IN REFINERY; HENCE, FOR THE SAKE OF SIMPLICITY, THEY ARE NOT SHOWN HERE.

Figure D-3. SCOT Process

2.3 Feed Stream Requirements

Temperature: 400°K - 430°K (260°F - 320°F)

Pressure: 0.13 MPa (19 psia)

2.4 Operating Parameters

2.4.1 Catalytic Reactor

Temperature: 573°K (572°F)(3)

Pressure: ~0.13 MPa (~19 psia)

2.4.2 Gas Treatment, Amine Absorber

Temperature: 310°K - 320°K (100°F - 120°F)

Pressure: approximately atmospheric

2.5 Process Efficiency and Reliability(3,6) - In situations where the Claus tail gas sulfur content is about 9000 ppm (as SO_2), typical of a Claus unit with 94% sulfur recovery, the SCOT system can reduce the sulfur level in the gas to less than 250 ppm (as SO_2).

Maintenance is reportedly low, stream factor high.

2.6 Raw Material Requirements(6)

Catalyst: coablt molybdate based, three or more years lifetime

Diisopropanolamine: replacement for mechanical losses only

2.7 Utility Requirements (for a 100 tonne/day Claus plant(5))

- Electricity: 140 kwh/hr
- Fuel Gas: 1,224 Nm^3/min (45,600 scfm), based on 9000 kcal/m^3 (1012 Btu/ft^3)
- Cooling Water: (6.7°C, 12°F rise): 82 l/sec (1300 gpm)
- Steam (3.4 atm. sat): 1,162 kg/hr (2560 lb/hr) net. Steam is produced in the catalytic reactor (2,588 kg/hr) and consumed in the amine regenerator (3,750 kg/hr).

3.0 Process Advantages(3,4)

- Utilizes standard sulfur recovery equipment.
- Easily adapted to existing Claus plants.

- Process produces some of its steam requirements.
- Process can adapt to variations in feed stream composition.
- Can be integrated with bulk acid gas removal unit (e.g., ADIP for Claus feed upgrading and tail gas cleanup).

4.0 Process Limitations(1,2,3)

- Requires some type of fuel gas to supply heat and a reducing gas for the catalytic reaction.
- The SCOT system is utilized for the treatment of Claus plant tail gas; hence, if sulfur recovery is conducted by means other than the Claus process, SCOT system may be an inappropriate choice for tail gas treatment.
- Like other catalytic processes, the efficiency of conversion of COS and CS_2 to H_2S is decreased when high levels of CO_2 are present in Claus plant tail gas.

5.0 Process Economics(1)

For capital and operating costs (1972 dollars) for the various sized SCOT units, see Table D-3.

6.0 Input Stream

- Feed gas stream, Claus Tail Gas, Stream 1, see Table D-4.
- Hydrogen stream, Stream 7: 9.5 kg/hr (21 lb/hr) pure hydrogen required for 100 tonne/day Claus plant(5).
- Fuel gas, Stream 9: 1,224 Nm^3/min (45,660 scfm), based on 9000 kcal/m^3 (1012 Btu/ft^3) for 100 tonne/day Claus plant(5).
- Catalyst makeup: typically three or more years lifetime.
- Amine makeup: depends primarily on mechanical losses.

7.0 Discharge Streams

- Tail gas from process, Stream 2, see Table D-4.
- Condensate, Stream 14: Slightly acidic, H_2S and CO_2 dissolved to about 50 ppm each. 0.44 - 0.63 l/sec (7-10 gpm) for 100 tonne/day Claus plant(5).
- Spent catalyst: ?

TABLE D-3. CAPITAL AND OPERATING COSTS FOR VARIOUS SIZED SCOT UNITS (IN 1972 DOLLARS)*

	Add-On SCOT Unit[‡]			Integrated SCOT Unit[§]		
	Capacity of Claus unit, ton of S intake/sd					
	100	200	1,000	100	200	1,000
Total capital investment, US $ x 10^6[†]	0.9	1.6	3.6	0.7	1.2	2.8
Operating costs, $/stream day (333 stream days/annum):						
Direct costs	270	460	1,880	270	460	1,880
Capital charge (17% on equipment capital)	450	770	1,680	370	570	1,280
Totals	720	1,230	3,560	640	1,030	3,160

*The capital investment for the add-on SCOT unit corresponds to about 100% of the capital investment of the preceding Claus unit. For the integrated SCOT unit it is about 75%.

[†] Basis: West Europe; for the USA these figures should be increased by 10%.

[‡] Add-on: SCOT unit with gas blower, separate alkanolamine regeneration facilities and separate sour water stripper.

[§] Integrated: SCOT unit fully integrated but bearing a share of the costs for combined amine regeneration facilities and sour water stripper. There is no gas blower but the costs of pressure increase in upstream units has been added.

TABLE D-4. TYPICAL GAS STREAM COMPOSITION FOR SCOT PROCESS(1)

Components	Claus Tail-Gas to SCOT vol %	SCOT Tail-Gas to Atmosphere vol %
H_2S	0.85	0.03
SO_2	0.42	----
S_8 vapor and mist	0.05	----
COS	0.05	10 ppm
CS_2	0.04	1 ppm
CO	0.22	3.05
CO_2	2.37	<0.3
H_2O	33.10	7.00
N_2	61.30	88.96
H_2	1.60	0.96
Temperature	413^oK (284^oF)	313^oK (105^oF)
Pressure	0.15 MPa (22 psi)	0.1 MPa (14.7 psi)

8.0 Data Gaps and Limitations

- No information is available which would indicate applicability to coal conversion processes (e.g., the performance with high CO_2 levels in feed).

- The effect that various contaminants (NH_3, carbonaceous matter, trace metals, etc.) have on the process, and the ultimate fate of such contaminants in the system are unknown.

9.0 Related Programs

No information available.

REFERENCES

1. Gas Processing Handbook, Hydrocarbon Processing, April 1975.
2. Maddox, R. N., Gas and Liquid Sweetening, Campbell Petroleum Series, 1974.
3. Naber, J. E., J. A. Wesselingh, et al, New Shell Process Treats Claus Off-Gas, Chemical Engineering Progress, December 1973.
4. Beers, W. D., Characterization of Claus Plant Emissions, USEPA, NTIS No. PB-220 376, April 1973.
5. Battelle Columbus Laboratories, Characterization of Sulfur Recovery from Refinery Fuel Gas, USEPA, NTIS No. PB-239-777, June 1974.
6. Information provided to TRW by J. M. Duncan of Shell Development Company, December 8, 1977.

BEAVON PROCESS

1.0 General Information

1.1 Operating Principle(1) - The purification of sulfur plant tail gases by the catalytic conversion of sulfur species to H_2S followed by recovery of the H_2S as elemental sulfur in a Stretford unit. Fuel gas is used to supply heat and to produce a reducing gas for the catalytic reduction; cobalt molybdate is the catalyst employed.

1.2 Development Status - Commercially available.

1.3 Licensor/Developer - Union Oil Company
P. O. Box 218
Brea, California 92621

1.4 Commercial Applications - Approximately 30 Beavon units are in operation. They are used primarily for Claus unit tail gas treatment(1) and are presented in Table D-5.

2.0 Process Information

2.1 Flow Diagram (see Figure D-4)(2) - Tail gas from the sulfur plant, Stream 1, is mixed and combustion products and fed to a reactor containing cobalt molybdate catalyst. In the reactor sulfur species are converted to H_2S. The H_2S rich gas, Stream 5, flows to a condenser where it is cooled and then sent to a Stretford unit for conversion of H_2S to sulfur(3).

2.2 Equipment(1,2,3) - Conventional burner, catalytic reactor, coolers, absorber, oxidation tank, surge tank.

2.3 Feed Stream Requirements

Temperature: typically $390^{o}K$-$420^{o}K$ ($250^{o}F$-$300^{o}F$)

Pressure: 0.116-0.122 MPa (17-18 psia)

TABLE D-5. BEAVON SULFUR REMOVAL PROCESS (BSRP) COMMERCIAL INSTALLATIONS(7)

Customer and Location	Claus Capacity (LTPD)	BSRP Units
Atlantic Richfield Company Philadelphia, Pennsylvania	140	1
Cities Service Oil Company Lake Charles, Louisiana	307	3*
The Dow Chemical Company Freeport, Texas	450	2
Exxon Company, U.S.A. Baton Rouge, Louisiana	300	1
Exxon Company, U.S.A. Baytown, Texas	300	1
Exxon Company, U.S.A. Baytown, Texas	1116	2
Exxon Company, U.S.A. Bayway, New Jersey	300	1
General Sekiyu Seisei Sakai, Japan	150	1
Getty Oil Company Delaware City, Delaware	342	1
Hess Oil Virgin Islands Corp. St. Croix, Virgin Islands	300	1
Hess Oil Virgin Islands Corp. St. Croix, Virgin Islands	320	1
Marathon Oil Company Garyville, Louisiana	232	2*
Mobil Oil Corp. Paulsboro, New Jersey	270	2
Mobil Oil Corp. Torrance, California	200	2

(continued)

*Employs 1 Stretford unit only.

TABLE D-5. Continued

Customer and Location	Claus Capacity (LTPD)	BSRP Units
Nihon Ryutan Kogyo K.K. Tsurusaki, Japan	180	1
Texaco, Inc. Long Beach, California	350	1
Toa Oil Company, Ltd. Kawasaki, Japan	320	2
Union Oil Company of California Chicago, Illinois	300	2*
Union Oil Company of California Los Angeles, California	200	2
Union Oil Company of California Rodeo, California	245	3
Wintershall AG Lingen, Germany	75	1†

*Employs 1 Stretford unit only.
†Employs Selectox process.

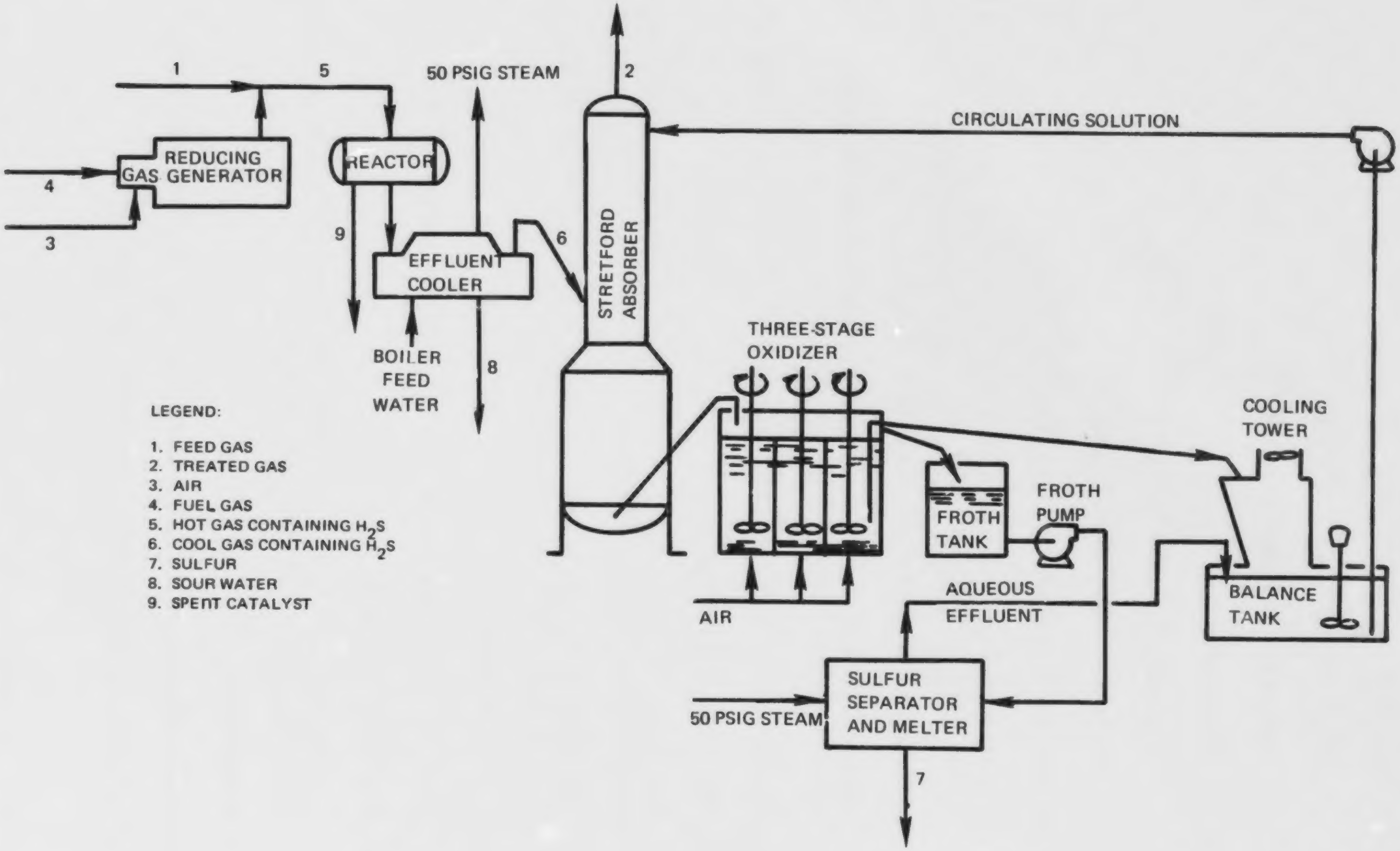

1
5
50 PSIG STEAM
2
CIRCULATING SOLUTION
4
3
REDUCING GAS GENERATOR
REACTOR
9
6
EFFLUENT COOLER
STRETFORD ABSORBER
BOILER FEED WATER
8
THREE-STAGE OXIDIZER
COOLING TOWER
FROTH TANK
FROTH PUMP
AQUEOUS EFFLUENT
BALANCE TANK
AIR
SULFUR SEPARATOR AND MELTER
50 PSIG STEAM
7
LEGEND:
1. FEED GAS
2. TREATED GAS
3. AIR
4. FUEL GAS
5. HOT GAS CONTAINING H_2S
6. COOL GAS CONTAINING H_2S
7. SULFUR
8. SOUR WATER
9. SPENT CATALYST

Figure D-4. Beavon Process

2.4 Operating Parameters

2.4.1 Reactor

Temperature: 644°K (700°F)(3)

Pressure: 0.1 MPa (1 atm)(6)

2.4.2 Condenser

Temperature: 310°K (100°F)(6)

Pressure: 0.1 MPa (1 atm)(6)

2.5 Process Efficiency and Reliability(4,7)

- In refinery applications where the Claus tail gas contains about 4% equivalent H_2S, the tail gas from the Beavon process will contain less than 40 ppm equivalent SO_2* (COS constituting major portion and H_2S will be less than 1 ppm).
- Process involves basic refinery technology and is generally insensitive to feed stream upset conditions.
- No unusual maintenance or hazardous conditions are reported.

2.6 Raw Material Requirements

- Fuel gas: 37000 Nm^3/day per tonne (1.25 MSCFD/ton) of parent sulfur plant capacity(2).
- Stretford Solution Alkali: 0.013 to 0.06 l/sec (0.21 to 1.0 gpm) for 100 tonne per day Claus plant(6,7).

2.7 Utility Requirements

- Power: 70 kwh per tonne (64 kwh/ton) of sulfur in the tail gas(2).
- Fuel gas: no data available
- Cooling water: 22.7 l/sec (360 gpm) for 100 tonne per day Claus plant(6). (Air cooling can be used.)

3.0 Process Advantages(1,5)

- Recovers organic sulfur compounds and SO_2 as elemental sulfur.
- Can utilize existing Stretford plant, if available.

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*Union guarantees 100 ppmv for refinery applications.

- Equipment can be constructed of carbon steel with certain items being treated with epoxy coating.
- Process is basically insensitive to variations in feed stream compositions.
- Process produces approximately 80 kg/hr (175 lb/hr) of 0.43 MPa (65 psia) steam per ton of sulfur in tail gas(7).

4.0 Process Limitations(2,3)

- High fixed cost of facility including royalty fees.
- Requires some type of fuel gas to supply heat and to produce a reducing gas for the catalytic reaction.
- Like other catalytic processes, efficiency of conversion of COS and CS_2 to H_2S is decreased if high levels of CO_2 are present in Claus plant tail gas.

5.0 Process Economics(2)

- Costs as reported in 1972 are as follows:
  - Fixed costs including royalties

1% Sulfur Equivalent in Feed Gas

Parent Sulfur Plant Capacity tonne (long ton) per day	Investment $ Million
1.11 (1)	0.69
11.1 (10)	1.40
111 (100)	5.80*

4% Sulfur Equivalent in Feed Gas

Parent Sulfur Plant Capacity tonne (long ton) per day	Investment $ Million
1.11 (1)	0.61
11.1 (10)	1.20
111 (100)	3.55†

  - Operating costs(7): approximately $40 per long ton sulfur in tail gas per day.

---

*Multiple hydrogenation and Stretford trains.
†Multiple Stretford trains.

6.0 Input Streams(4,7)

- Feed gas stream, Claus tail gas (Stream 1) see Table D-6.
- Fuel gas (Stream 4): sufficient to heat Stream 1 from 400°K to 620°K (270°F to 650°F)
- Air (Stream 3): 80%-90% of stoichiometric requirements for fuel gas
- Chemical and catalyst makeup: ADA, vanadium, and caustic soda

7.0 Intermediate Streams(6)

- Reactor offgas (Stream 5)-see Table D-7.
- Condenser offgas (Stream 6)-see Table D-7.

8.0 Discharge Stream

- Tail gas from process (Stream 2)-see Table D-6.
- Sour water (Stream 8): pH - slightly acidic; H_2S and CO_2 - dissolved to about 50 ppm each(6). In refineries sour water is recycled to existing sour water strippers.

9.0 Data Gaps and Limitations

Data gaps exist in the following areas:

- Process applicability to coal conversion process gas purification systems has not been established, particularly for processing high CO_2 Claus tail gases.†
- Characterization of gaseous and liquid feed and discharge streams for refinery applications (temperature, pressure, composition, etc.).
- The effect that various contaminants (NH_3, HCN, carbonaceous matter, trace metals, etc.) have on the process, and the ultimate fate of such contaminants in the system.

10.0 Related Programs: No data available.

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*Nature of the chemicals not given.

†Union has indicated that Beavon systems can be guaranteed to achieve 250 ppmv total sulfur in coal gasification applications(8).

TABLE D-6. TYPICAL BEAVON GAS STREAM COMPOSITION IN REFINERY APPLICATIONS(4)

Components	Claus Tail Gas to Beavon	Beavon Tail Gas
H_2S	2.0%	0.0%
SO_2	1.0%	0%
S	0.7%	0.0%
COS	0.3%	<250 ppm*
CS_2	0.3%	0.0%
CO_2	10%	14%
H_2O vapor	26%	5%
N_2	56%	80.8%
H_2	2.5%	varies
CO	1.0%	0.2%

*Union guarantees 100 ppmv; typically 40 ppmv is attained(7).

TABLE D-7. TYPICAL COMPOSITION OF BEAVON INTERMEDIATE GAS STREAMS*(6,7)

Components (vol %)	Claus Tail Gas to Beavon	Reactor Offgas	Condenser Offgas
H_2S	0.85	1.54	2.13
SO_2	0.42	0.00	0.00
S	0.05	0.00	0.00
COS	0.05	40 ppm	40 ppm
CS_2	0.04	2 ppm	2 ppm
CO_2	2.37	3.18	4.39
H_2O vapor	33.10	32.30	6.45
N_2	61.30	62.50	86.36
H_2	1.60	0.21	0.29
CO	0.22	0.20	0.28
HC (MW=30)	--	0.06	0.08
Temperature	413°K (284°F)	673°K (752°F)	311°K (100°F)
Pressure	0.126 MPa (18.5 psia)	0.1 MPa (14.7 psia)	0.1 MPa (14.7 psia)

*Based on the Claus tail gas composition given above for a 100 tonne per day Claus plant.

REFERENCES

1. Gas Processing Handbook, Hydrocarbon Processing, April 1975.

2. Beers, W. D., Characterization of Claus Plant Emissions, USEPA, NTIS No. PB-220-376, April 1973.

3. Maddox, R. N., Gas and Liquid Sweetening, Campbell Petroleum Series, 1974.

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5. New Beavon Process Takes Sulfur-Bearing Compounds from Tail Gas, Oil and Gas Journal, 70 (6), 1972.

6. Battelle Columbus Laboratories, Characterization of Sulfur Recovery from Refinery Fuel Gas, U.S. EPA, NTIS No. PB-239-777, June 1974.

7. Information provided to TRW by G. E. Tilley of Union Oil Company, June 14, 1978.

8. Letter, G. L. Tilley, Union Oil Research, to C. B. Sedman of Emission Standards and Engineering Division, Office of Air Quality Planning and Standards of EPA, January 2, 1976.

INSTITUT FRANCAIS DU PÉTROLE (I.F.P.) PROCESS

1.0 General Information

1.1 Operating Principle(1) - The removal of sulfur compounds from Claus tail gas by catalyticly reacting the H_2S with SO_2 (the basic Claus reaction: $2H_2S + SO_2 = 3S + 2H_2O$) in a solvent. The solvent is generally an alkaline earth metal salt of a carboxylic acid.

1.2 Development Status - Commercially available.

1.3 Licensor/Developer - Institut Francais du Pétrole
1 et 4, av. de Bois-Preau
92-Rueil-Malaison
(Hauts-de-Seine) France

1.4 Commercial Applications(2) - Claus plant tail gas treatment; approximately 25 plants in operation or in various stages of planning, design or construction. Operating plants are located throughout the world. Table D-8 gives some specific information on four plants in Japan and a demonstration plant in Canada.

2.0 Process Information

2.1 Flow Diagram (see Figures D-5 and D-6)*

- Figure D-5 illustrates the IFP-1 flow diagram. The Claus tail gas, Stream 1, is injected into a packed tower, counter-currently contacting the solvent containing catalyst. Sulfur, Stream 3, is formed, collected and removed from the tower, and the treated gas, Stream 2, is sent to an incinerator where the remaining sulfur compounds (H_2S, COS, CS_2) are converted to SO_2.

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*There are two IFP processes: one process, IFP-1, removes H_2S and SO_2 from Claus tail gas to a SO_2 equivalent level of 1500 to 2000 ppm; the other process, IFP-2, removes H_2S and SO_2 from Claus tail gas to an SO_2 equivalent level of less than 500 ppm.

TABLE D-8. I.F.P. PROCESS PLANT LOCATIONS AND APPLICATION(3)

Plant Owner	Location	Application	Through-put Nm^3/D (MMSCFD)	Sulfur Recovery Rate (%)
Delta Engineering Corp.	Lone Pine Alberta	Demonstration Plant	21,500 (0.8)	80 - 85
Nippon Petroleum Refining Company	Negishi Japan	Cleaning tail gas from 3-stage Claus plant	699,400 (26)	85
Idemitsu Oil Co.	Japan	Cleaning tail gas from 3-stage Claus plant	592,000 (22)	85
Kyokutoh Oil Co.	Japan	Cleaning tail gas from 3-stage Claus plant	406,400 (16)	90
Showa Oil Co.	Japan	Cleaning tail gas from 3-stage Claus plant	113,000 (4.2)	85

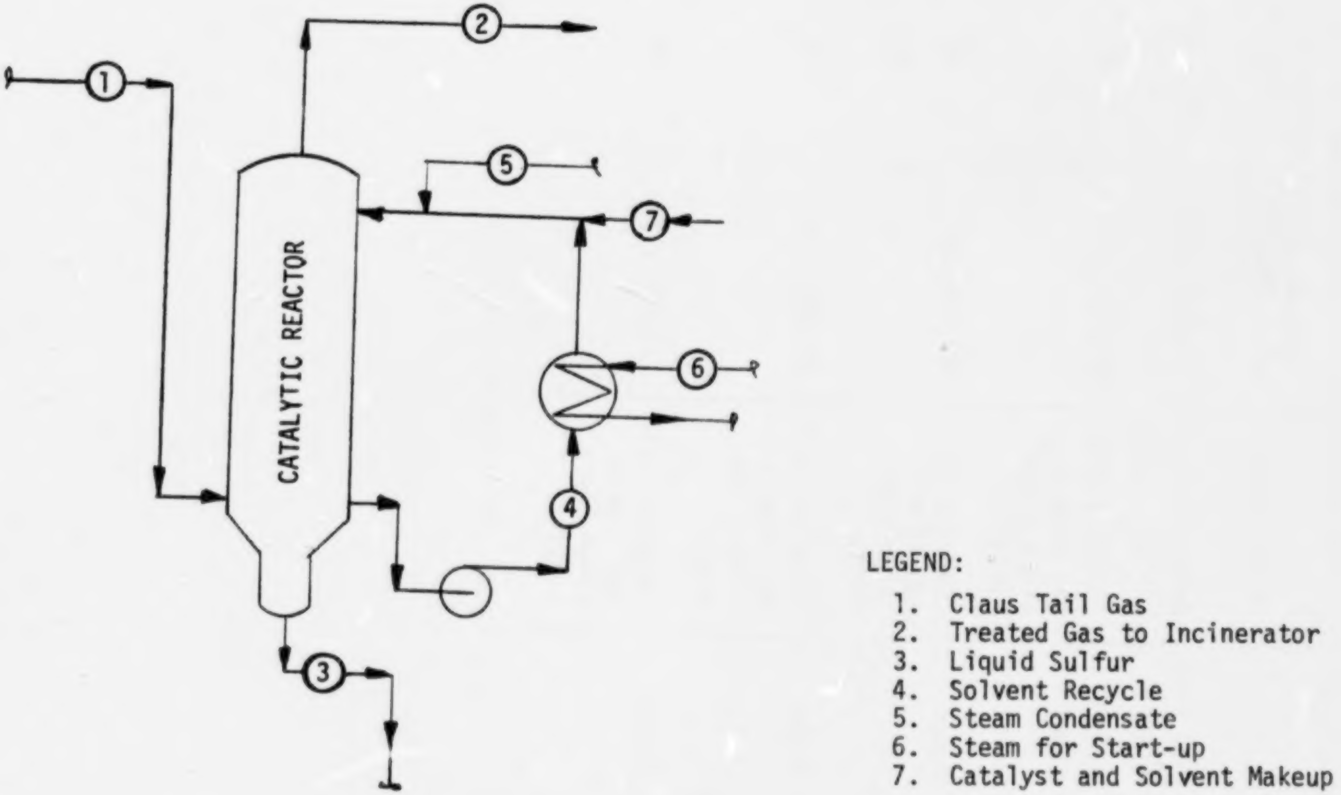
②
①
⑤
⑦
CATALYTIC REACTOR
⑥
④
③
LEGEND:
1. Claus Tail Gas
2. Treated Gas to Incinerator
3. Liquid Sulfur
4. Solvent Recycle
5. Steam Condensate
6. Steam for Start-up
7. Catalyst and Solvent Makeup

Figure D-5. Institut Francais du Pétrole Process (IFP-1)

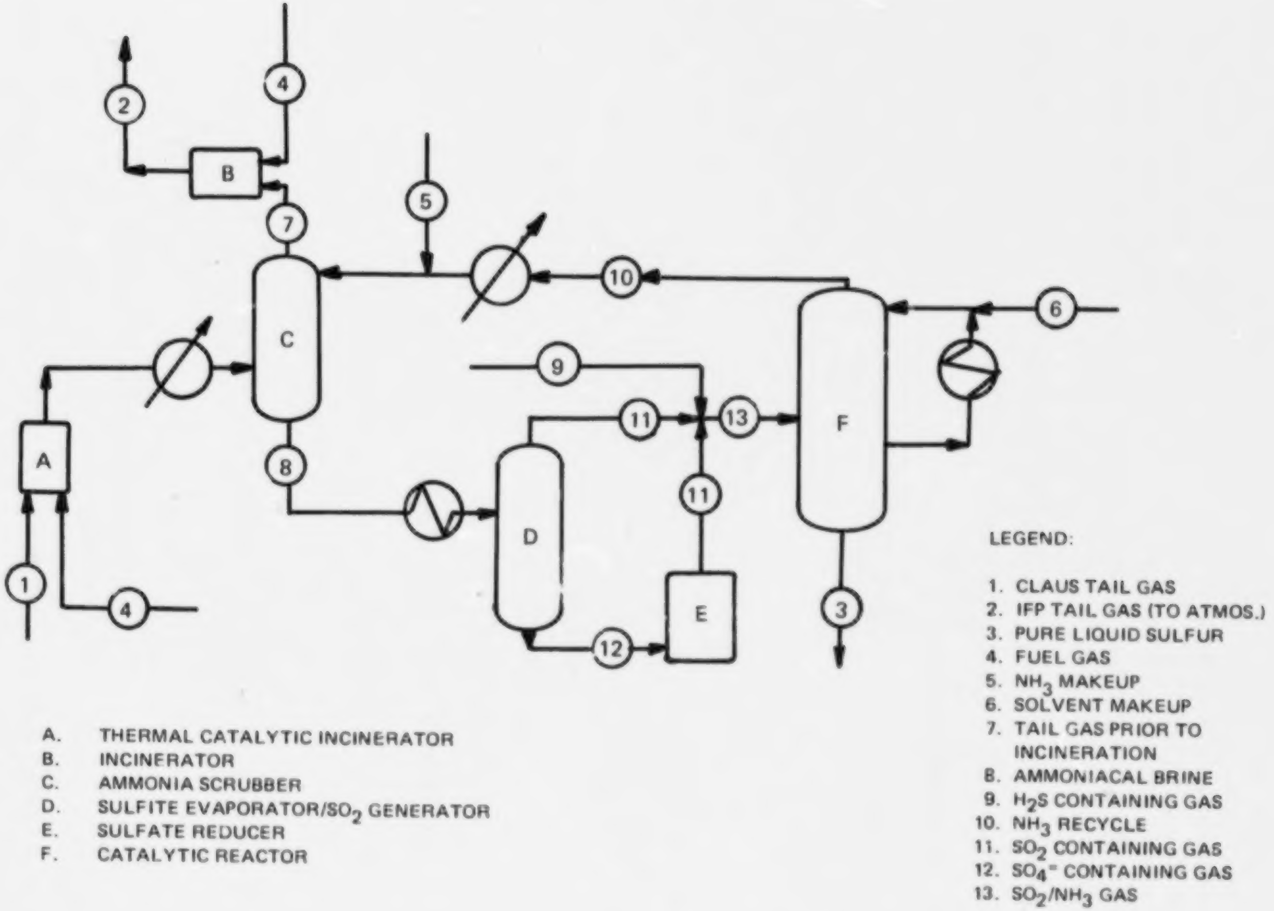
2
4
B
7
5
10
C
6
9
11
13
F
A
8
D
11
1
4
E
3
12
A. THERMAL CATALYTIC INCINERATOR
B. INCINERATOR
C. AMMONIA SCRUBBER
D. SULFITE EVAPORATOR/SO_2 GENERATOR
E. SULFATE REDUCER
F. CATALYTIC REACTOR
LEGEND:
1. CLAUS TAIL GAS
2. IFP TAIL GAS (TO ATMOS.)
3. PURE LIQUID SULFUR
4. FUEL GAS
5. NH_3 MAKEUP
6. SOLVENT MAKEUP
7. TAIL GAS PRIOR TO INCINERATION
8. AMMONIACAL BRINE
9. H_2S CONTAINING GAS
10. NH_3 RECYCLE
11. SO_2 CONTAINING GAS
12. $SO_4^{=}$ CONTAINING GAS
13. SO_2/NH_3 GAS

Figure D-6. Institut Francais du Pétrole Process (IFP-2)

- Figure D-6 illustrates the IFP-2 flow diagram. The Claus tail gas, Stream 1, is incinerated, then scrubbed with an aqueous ammonia solution. The scrubbed gas, Stream 7, is incinerated prior to release to the atmosphere. Ammonical brine, Stream 8, is piped to a sulfite evaporator/SO_2 generator and then to a sulfate reducer unit. SO_2/NH_3 streams, produced in the sulfite evaporator/SO_2 generator and the sulfate reducer, are combined with a supplementary H_2S stream (Stream 9) and the combined stream (Stream 13) is sent to a catalytic reactor for Claus reaction. The product liquid sulfur, Stream 3, is piped away and ammonia, Stream 10, is recycled.

2.2 Equipment - Conventional absorbers, evaporators, catalytic reactor, scrubbers, incinerator, and thermal catalytic incinerator.

2.3 Feed Stream/Requirements

Temperature: 400°K - 415°K (265°F - 285°F) maximum for IFP-1 without cooling(16).

Pressure: ?

Others: ?

2.4 Operating Parameters

2.4.1 Scrubber - Temperature: ?
Pressure: ?
Solvent loading: ?
Other: ?

2.4.2 Sulfite Evaporator/SO_2 Generator - Temperature: ?
Pressure: ?
Solvent loading: ?
Other: ?

2.4.3 Catalytic Reactor - Temperature: 393°K - 403°K (248°F - 266°F)(6).
Pressure: ?
Solvent/catalyst loading: ?
Other: ?

2.5 Process Efficiency and Reliability - IFP-2 process is reported to be capable of removing sulfur species in Claus tail gas to 500 ppm or less as SO_2. IFP-1 is capable of removing sulfur species in Claus tail gas to 1500 to 2000 ppm as SO_2(2). No information is available as to the reliability of the process.

2.6 Raw Material Requirements - No information is available as to the quantity of makeup ammonia, polyalkaline glycol and catalyst requirements.*

2.7 Utility Requirements†

- Electricity: 35 kwh/hr for IFP-1 process applied to a 100 tonne/day Claus plant(6).
- Fuel gas: ?
- Water: ?
- Others: ?

2.8 Miscellaneous - No information available which indicates special maintenance problems or unusual hazardous conditions created by the process.

3.0 Process Advantages

- Solvent and catalyst are readily available at a low cost(3,4).
- Produces high quality sulfur.
- Low foaming tendency of solvent.
- Minimum solvent loss due to its low vapor pressure(3,4).
- Catalyst is highly active(3,4).
- Both solvent and catalyst are chemically and thermally stable(3,4).
- Carbon steel can be used throughout process(5).
- The total H_2S + SO_2 concentration in the feed gas has little effect on investment cost(4).

---

*The solvent and catalyst makeup costs for an IFP-1 process are reported to be approximately $350 per day for a 1274-tonne (1400-ton) per day Claus plant(2). Further, the solvent and catalyst makeup cost for an IFP-2 process is approximately $5 per day for a 228-tonne (250-ton) per day Claus plant(2).

†The utility cost for an IFP-1 process is reported to be approximately $30 per day for a 1274-tonne (1400-ton) per day Claus plant(2). Also, the utility cost for an IFP-2 process is approximately $70 per day for a 228-tonne (250-ton) per day Claus plant(2).

- IFP process can be made up of a combination of remote unit locations and central plant to optimize capital investment*(5).

- Investment is small in comparison with the cost of the Claus plant.

- Does not create any water pollution(5).

4.0 Process Limitations

- For optimum operating conditions, the H_2S/SO_2 ratio in the feed to the catalytic reactor should be maintained in the range of 2.0 to 2.4(3).

- COS and CS_2, if present, are not removed in the catalytic reactor(5).

- Tail gas must be incinerated prior to release to the atmosphere via stacks(3).

- No commercial applications reported for the process other than Claus tail gas cleanup.

5.0 Process Economics

- The overall cost of a 182-tonne/day (200-ton/day) sulfur plant is approximately $2.00 per 1000 Nm^3 ($53.00/MMSCF) of tail gas treated(5).

6.0 Input Streams

- Feed stream, Claus tail gas, Stream 1, see Table D-9.

- NH_3 makeup, Stream 5, Figure D-6: ?

- Fuel gas, Stream 4, Figure D-6: ?

- Solvent catalyst makeup, Stream 6, Figure D-6: ?

7.0 Discharge Streams

- IFP tail gas prior to incineration, Stream 2, Figure D-5, see Table D-9.

- Production sulfur, Stream 3, see Table D-9.

- IFP tail gas prior to incineration, Stream 2, Figure D-5; and after incineration, see Table D-10.

8.0 Data Gaps and Limitations

- Input and discharge stream data supplied above is for IFP-1 process; no stream information was available for the IFP-2 process.

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*This is a desirable feature in applications where Claus plants are located at different locations in a major facility or in several near-by plants.

TABLE D-9. THREE APPLICATIONS OF THE IFP-1 PROCESS FOR TREATING CLAUS TAIL GAS(4)*

Stream Composition/ Operating Conditions	Treating Tail Gas After		
	One-Stage Claus	2-Stage Claus	3-Stage Claus
Claus Tail Gas Composition Stream 1, Mole %:			
H_2S	1.48	0.59	0.34
SO_2	0.74	0.29	0.17
S	1.26	0.14	0.13
H_2O	28.58	24.96	30.25
N_2, CO_2, Misc.	67.94	69.02	69.11
Temperature, °K (°F)	400 (260)	400 (260)	400 (260)
Pressure, MPa (psig)	0.10 (0.50)	0.10 (0.50)	0.10 (0.50)
Sulfur Recovery			
$H_2S + SO_2$ reaction, %	95	90	80
Production Rate (Stream 3), kg/hr (lb/hr)	112.3 (247)	36.8 (81)	19.5 (43)
Treated gas to incinerator, Stream 7, ppm of $H_2S + SO_2$	1100	900	1000

*Refer to Figure D-5.

TABLE D-10. TYPICAL COMPOSITION OF GAS STREAMS FOR THE IFP-1 PROCESS FOR TREATING CLAUS TAIL GAS*(6)

Components (vol %)	Claus Tail Gas to IFP	After Catalytic Reactor	After Incinerator
H_2S	0.85	0.085	--
SO_2	0.42	0.042	0.212
S	0.05	0.040	--
COS	0.05	0.040	--
CS_2	0.04	0.075	--
CO	0.22	0.219	--
CO_2	2.37	2.376	4.483
H_2	1.60	1.607	--
H_2S	33.10	33.990	30.502
N_2	61.30	61.545	64.299
O_2	--	--	0.504
Temperature	413°K (285°F)	392°K (246°F)	923°K (1200°F)
Pressure	0.126 MPa (18.5 psia)	0.1 MPa (14.7 psia)	0.1 MPa (14.7 psia)

*Based on the tail gas composition given above for a 100-tonne per day Claus plant.

- Data gaps exist in the following areas:
  - Applicability of the process to coal conversion processes; e.g., efficiency, reliability, feed stream requirements.
  - Characterization of gaseous and liquid streams (e.g., purified gas, feed gas) for the IFP-2 process in commercial refinery gas treating application.
  - Definition of the maximum allowable concentrations of various contaminants in the feed gas; e.g., COS, CS_2, trace metals, carbonaceous matter.
  - The effect that various contaminants (trace metals, carbonaceous matter, COS, CS_2, HCN) have on the process, and the ultimate fate of such contaminants in the system.

9.0 Related Programs

No data available.

REFERENCES

1. Maddox, R. N., Gas and Liquid Sweetening, Campbell Petroleum Series, 1974.
2. Gas Processing Handbook,Hydrocarbon Processing, April 1975.
3. Beer, W. D., Characterization of Claus Plant Emissions, U.S. EPA, NTIS PB-220-376, April 1973.
4. Barthel, Y., Y. Bistri, et al, Treat Claus Tail Gas, Hydrocarbon Processing, May 1971.
5. Bonnifay, P., R. Dutrian, et al, Partial and Total Sulfur Recovery, Chemical Engineering Progress, Vol. 68, No. 8, August 1972.
6. Battelle Columbus Laboratories, Characterization of Sulfur Recovery from Refinery Fuel Gas, U.S. EPA, NTIS No. PB-239-777, June 1974.

SULFREEN PROCESS

1.0 General Information

1.1 Operating Principles(1,2,3,4,5) - SO_2 and H_2S in Claus tail gas are removed by further promotion of the Claus reaction on a catalytic surface. This process was designed specifically for treatment of tail gases of Claus type sulfur plants, either in gas processing plants or refineries. The reaction is carried out in a solid batch reactor utilizing an activated alumina catalyst. Adsorbed sulfur is desorbed with hot Claus tail gas (circulating in a closed loop system) from which the sulfur vapor is removed in a condenser-coalescer.

1.2 Licensor/Developer - Developed by Lurgi Gesellshaft for Warme and Chemotechnic (Lurgi) of West Germany and Societe Nationale des Petroles D'Aquitaine (SNPA) of France. In addition to Lurgi and SNPA, the process is licensed to:

Ralph M. Parsons Company, Pasadena, California
Fluor Engineers and Constructors, Inc., Irvine, Calif.
Ford, Bacon & Davis, Dallas, Texas
Partec Lavalin, Inc., Calgary, Alberta, Canada

1.3 Commercial Status Application - Commercially available. Sixteen commercial scale plants treating sulfur plant tail gas have been constructed.

2.0 Process Information

2.1 Flow Diagram (see Figure D-7(1,4)) - Claus tail gas (Stream 1) is introduced in parallel into a battery of catalytic reactors where the Claus reaction is carried out at 130°C to 160°C (265°F to 320°F). This temperature is lower than that used in a Claus process, and the formation of elemental sulfur is favored. A battery of six reactors is shown in Figure D-7; four are utilized for sulfur adsorption, one

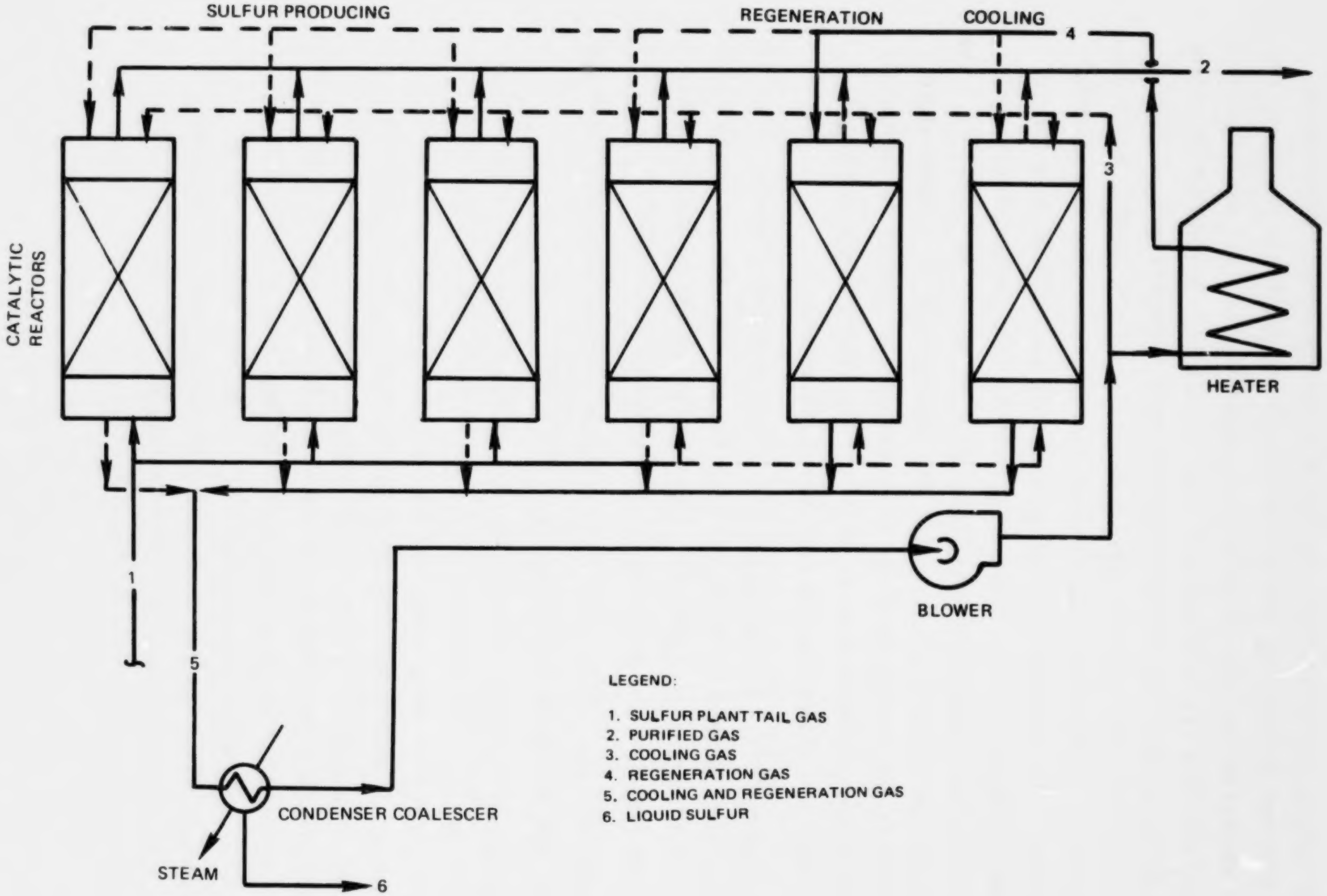
SULFUR PRODUCING
REGENERATION
COOLING
4
2
3
CATALYTIC REACTORS
HEATER
1
5
BLOWER
CONDENSER COALESCER
STEAM
6
LEGEND:
1. SULFUR PLANT TAIL GAS
2. PURIFIED GAS
3. COOLING GAS
4. REGENERATION GAS
5. COOLING AND REGENERATION GAS
6. LIQUID SULFUR

Figure D-7. Sulfreen Process Flow Diagram for catalyst regeneration, and one for cooling after regeneration. A Sulfreen process may consist of only three catalytic reactors, two in adsorption and one in desorption, depending on tail gas composition and flow rate and economic considerations. Desorption of sulfur from the catalyst is achieved by heating a regeneration gas (Stream 4), usually tail gas from the Claus unit, to 320°C (608°F) and circulating it through the catalyst bed, thereby vaporizing the adsorbed sulfur. The vaporized sulfur is condensed and removed from the regeneration gas in the condenser-coalescer. The condenser-coalescer reduces the regeneration gas temperature to about 120°C (248°F). The cooled gas is utilized to reduce the catalyst bed to a temperature suitable for adsorption after the regeneration process is completed. The process operates continusouly and the reactors are sequenced between the adsorption and desorption processes.

2.2 Equipment(2,4) - All equipment can be constructed of carbon steel if provision is made to maintain temperatures above the water dew point to avoid corrosion. However, stainless steel may be used for catalytic reactors and a portion of the regeneration circuit.

2.3 Catalyst Life(1,4) - Activated carbon or alumina catalyst is expected to have a life of approximately 4 to 6 years.

2.4 Process Efficiency - Capable of 80% to 85% removal of sulfur from tail gas(1). The Sulfreen unit operating at LACQ, France is 75% efficient(2). When using ordinary alumina catalyst, 80% sulfur removal is obtained, with combined H_2S and SO_2 concentration of 2000-2500 ppm in the treated gas stream. Overall sulfur removal efficiencies for Claus and Sulfreen are in the range of 98.5% to 99%. A promoted activated alumina has been developed by Lurgi and SNPA to prevent poisoning by sulphation and aging. Overall sulfur removal efficiency for Claus and Sulfreen of 99.5% is obtained, with combined H_2S and SO_2 concentration of 1000-1200 ppm. Very good conversion of COS is also obtained.

2.5 Chemical Requirements(1) - (Based on 100 tonne per day Claus unit)

- Catalyst alumina: 11.0 kg/hr (24.3 lb/hr)
- Nitrogen: 44.9 Nm^3/hr (1675 scf/hr)

2.6 Utility Requirements(1) - (Based on 100 tonne per day Claus unit and alumina catalyst)

- Steam produced in process (0.48 MPa, 70 psia saturated): 735 kg/hr (1620 lb/hr)
- Electricity: 124 kwh/hr
- Fuel Gas: 60.9 Nm^3/hr (2272 scf/hr)
- Boiler feed water: 0.189 l/sec (3.0 gpm)

3.0 Process Advantages

- Process does not have a major liquid waste stream(1).
- Produces high quality sulfur - 99.9% pure(3).
- Alternating catalytic reactors between adsorption and desorption permits continuous operation(2).

4.0 Process Limitations

- CS_2 is not appreciably removed(1).
- Optimum performance requires a stoichiometric $H_2S:SO_2$ ratio of 2:1 in Claus tail gas, which necessitates careful control of Claus unit operations(2).
- Process designed specifically for Claus tail gas(2).

5.0 Process Economics(3,4)

A Sulfreen plant processing 110 MM SCFD of tail gas from a one million long ton per day sulfur plant was constructed for three million dollars. Operation and maintenance costs varied from $150,000 to $180,000 per year (1969 dollars). A Sulfreen plant processing 220,000 Nm^2/hr (197 MM SCFD) of tail gas from a 2,200 ton per day sulfur plant was constructed for 3.2 million dollars (Ram River Stage II, 1973 dollars).

6.0 Input Streams

6.1 Claus tail gas, prior to incinerator (Stream 1), see Table D-11.

TABLE D-11. TYPICAL GAS STREAM COMPOSITION FOR SULFREEN PROCESS (1)

Components (VOL %)	Claus Tail Gas Prior to Incineration	Purified Gas	Incinerated Sulfreen Tail Gas
H_2S	0.85	0.18	-
SO_2	0.42	0.085	3,385 ppm
S Vapor and Mist	0.05	0.013	-
COS	0.05	0.051	-
CS_2	0.04	0.04	-
CO	0.22	0.222	-
CO_2	2.37	2.39	2.9
H_2	1.60	1.62	-
H_2O	33.10	33.44	28.93
N_2	61.30	61.93	67.23
O_2	-	-	0.61
Temperature	140°C (284°F)	140°C (284°F)	650°C (1202°F)
Pressure	0.126 MPa (18.5 psia)	0.1 MPa (14.7 psia)	0.1 MPa (14.7 psia)

*Based on a 100 tonne per day Claus plant

NOTE: This stream data is considered to be out of date(6). However, it is the only data available at this time.

7.0 Discharge Streams

7.1 Purified gas (Stream 2), see Table D-11.

7.2 *Incinerated Sulfreen* tail gas, see Table D-11.

8.0 Data Gaps and Limitations

- No information which would indicate applicability to coal conversion processes.

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6. Information provided to TRW by Y. M. Philardeau of the Aquitaine Company of Canada Ltd., June 6, 1978.

CLEANAIR PROCESS

1.0 General Information

1.1 Operating Principles(1) - The purification of sulfur plant tail gases by catalytic conversions to H_2S, followed by a continuation of the Claus reaction and a Stretford unit where H_2S is recovered as elemental sulfur. A fixed-bed reactor contains both a reduction (possibly Co/Mo) and a hydrolysis (unknown) catalyst. The Claus reaction is promoted in a packed reactor with an unknown proprietary chemical solution.

1.2 Licensor/Developer - J. F. Pritchard Company
4625 Roanoke Parkway
Kansas City, Missouri 64112

1.3 Commercial Status/Application - Commercially available. Three units built in the U.S. remained on start-up status due to recurrent operating problems; two other units have been constructed in the U.S.S.R.

2.0 Process Information

2.1 Flow Diagram (See Figure D-8)(1,2,3) - A limited amount of information is available pertaining to specific details of the Cleanair process. The J. F. Pritchard Company apparently is reluctant to divulge specific process information. The process can be installed in three stages: the first stage converts SO_2 to sulfur; the second stage removes H_2S in a Stretford process; and the third stage converts COS and CS_2 to H_2S. The Stretford process offgas may be: incinerated in a typical Claus incinerator, converting residual H_2S to SO_2 and CO to CO_2; or discharged directly into the atmosphere.

2.2 Catalyst Life(2) - Catalyst life will generally vary from 2 to 5 years depending on plant operation and feed characteristics. High CO_2 concentrations will shorten catalyst life.

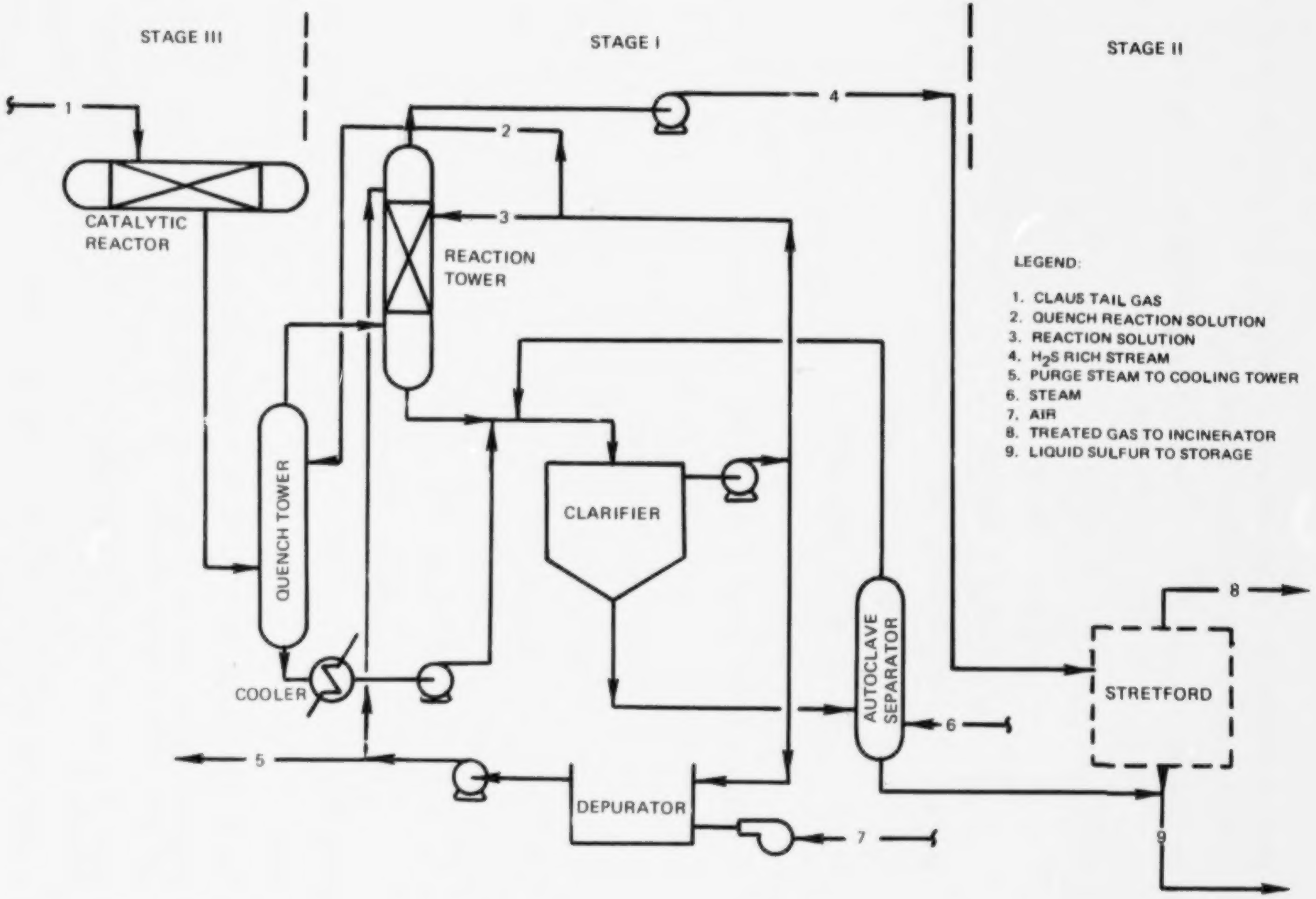
STAGE III
STAGE I
STAGE II
1
2
3
4
5
6
7
8
9
CATALYTIC REACTOR
REACTION TOWER
QUENCH TOWER
COOLER
CLARIFIER
DEPURATOR
AUTOCLAVE SEPARATOR
STRETFORD
LEGEND:
1. CLAUS TAIL GAS
2. QUENCH REACTION SOLUTION
3. REACTION SOLUTION
4. H2S RICH STREAM
5. PURGE STEAM TO COOLING TOWER
6. STEAM
7. AIR
8. TREATED GAS TO INCINERATOR
9. LIQUID SULFUR TO STORAGE

Figure D-8. Cleanair Process Flow Diagram

2.3 Process Efficiency - Plant effluent is normally guaranteed to contain less than 250 to 300 ppm of equivalent SO_2(2).

2.4 Utility Requirements(2,3) - (Claus unit capacities in long tons per day: *Case 1 = 50; Case 2 = 150; Case 3 = 500)*

- Electricity: Case 1 - 200 kw
  Case 2 - 580 kw
  Case 3 - 1900 kw
- Fuel Gas (8000 Kcal/m^3, 900 Btu/scf):
  Case 1 - 13.4 Nm^3/hr (500 scfh)
  Case 2 - 40 Nm^3/hr (1500 scfh)
  Case 3 - 121 Nm^3/hr (4500 scfh)
- Cooling Water (27.7°C, 80°F; 8.3°C, 15°F rise):
  Case 1 - 30. l/sec (475 gpm)
  Case 2 - 88. l/sec (1400 gpm)
  Case 3 - 287. l/sec (4550 gpm)
- Steam (0.44 MPa, 50 psig saturated):
  Case 1 - 181. kg/hr (400 lb/hr)
  Case 2 - 544. kg/hr (1200 lb/hr)
  Case 3 - 1814. kg/hr (4000 lb/hr)

3.0 Process Advantages(1,2)

- Produces high quality sulfur
- Can be adapted and retrofitted to existing Claus plants
- Provides flexibility in handling varying amounts of sulfur constituents (may vary threefold)
- H_2S : SO_2 ratio in the tail gas can vary up to 8:1 without affecting efficiency
- Potentially capable of very low sulfur emissions.

4.0 Process Limitations(1)

- Operational difficulties have been encountered
- High cost

5.0 Process Economics(2,3) - (1972 dollars)

- Capital investment: Case 1 - $ 925,000
  Case 2 - $1,400,000
  Case 3 - $2,200,000
- Annual operating and maintenance: Case 1 - $203,700
  Case 2 - $332,500
  Case 3 - $624,500

6.0 Input Streams

6.1 Feed Gas (Stream 1) - no data available

7.0 Waste Streams

7.1 Treated Gas (Stream 8) - no data available

7.2 Sour water stream purged from depurator (Stream 5) - no data available

8.0 Data Gaps and Limitations

- Disclosure of technical details of the Cleanair process requires completion of a secrecy agreement. Therefore, detailed stream data and process information are not available.
- No information which would indicate applicability to coal conversion processes.

9.0 Related Programs - none known

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Sulfur Oxides Control Module

Wellman-Lord

Chiyoda Thoroughbred 101

Shell Copper Oxide

Lime/Limestone Slurry Scrubbing

Dual Alkali

Magnesium Oxide Scrubbing

WELLMAN-LORD PROCESS

1.0 General Information

1.1 Operating Principles - Absorption of sulfur dioxide in a concentrated sodium sulfite solution followed by recovery of sulfur dioxide gas and solution regeneration.

1.2 Developmental Status - Commercially available.

1.3 Licensor/Developer - Developed by Davy-Powergas, Inc. (Lakeland, Florida), formerly Wellman-Lord, Inc.

1.4 Commercial Applications(1,2,3,9) - To date the commercial applications have been primarily for desulfurization of flue gas from fossil fuel-fired boilers. Systems in service include 14 oil-fired boilers in Japan and a 115-MW demonstration plant at the Mitchell Station of the Northern Indiana Public Service Company (the only application of process in coal-fired electric utility service). The most recent installation is on two 335-MW coal fired boilers in start-up operation at Public Service Co. of New Mexico at Farmington. The process would be applicable to the control of SO_2 emissions from other types of industrial operations and non-ferrous smelting, sulfuric acid and Claus plants. Twenty-five commercial installations are in current operation worldwide (all applications, including those for Claus plant and sulfuric acid plants). Possible applications in a commercial coal gasification facility may be in connection with support operations such as utility boilers and sulfur recovery (Claus plant tail gas treatment).

2.0 Process Information

2.1 Flow Diagram - see Figure D-9

- Process Description - The process can be viewed as composed of four major processing steps - flue gas pretreatment, SO_2

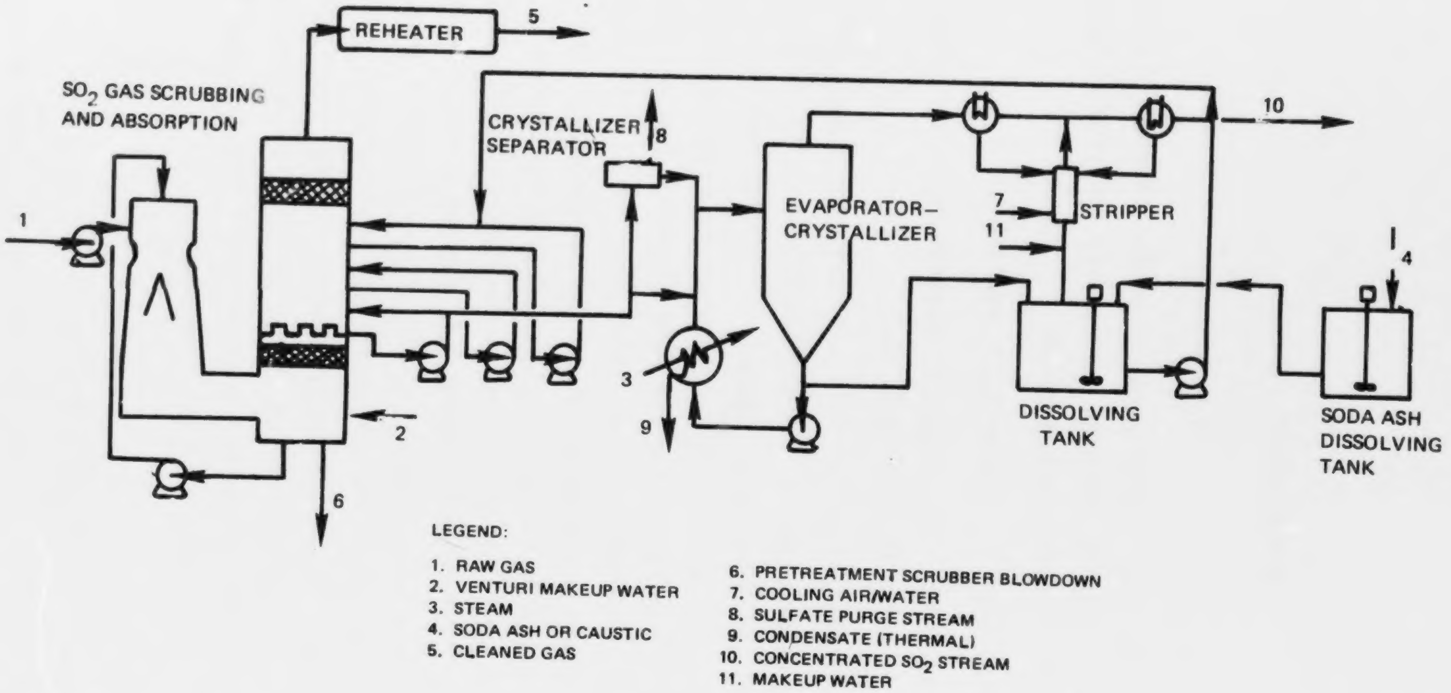
REHEATER
5
SO$_2$ GAS SCRUBBING AND ABSORPTION
CRYSTALLIZER SEPARATOR
8
10
1
EVAPORATOR–CRYSTALLIZER
7
11
STRIPPER
4
3
9
2
6
DISSOLVING TANK
SODA ASH DISSOLVING TANK
LEGEND:
1. RAW GAS
2. VENTURI MAKEUP WATER
3. STEAM
4. SODA ASH OR CAUSTIC
5. CLEANED GAS
6. PRETREATMENT SCRUBBER BLOWDOWN
7. COOLING AIR/WATER
8. SULFATE PURGE STREAM
9. CONDENSATE (THERMAL)
10. CONCENTRATED SO$_2$ STREAM
11. MAKEUP WATER

Figure D-9. Wellman-Lord Process Flow Sheet absorption, absorbent regeneration and purge treatment. See Table D-12 for brief descriptions of these processing steps.

2.2 Equipment(2,4) - see Table D-12.

2.3 Feed Stream Requirements

Pressure: Slightly above standard pressure.

Temperature: Normally designed to receive gas into the prescrubber at less than $533^{o}K$ ($500^{o}F$) and to receive saturated gas into the absorber at $311^{o}K$-$339^{o}K$ ($100^{o}F$-$150^{o}F$). Flue gas from utility boilers are usually somewhat less than $533^{o}K$.

Loading: Process can handle SO_2 concentrations well over 10,000 ppm.

Contaminant and Other Limitations(4): The system is very sensitive to the buildup of contaminants (sulfate, thiosulfate, and flyash). For applications to Claus plant tail gases it may be necessary to incinerate the gas to destroy H_2S, COS and CS_2 prior to SO_2 absorption, since these constituents tend to form thiosulfates which do not regenerate. The resultant sulfate levels are controlled at a level of about 5 wt % in the absorber feed by continuously purging sulfate at a rate equivalent to approximately 5%-10% of the absorbed sulfur value.

2.4 Operating Parameters

- Absorption

  Temperature: $310^{o}K$-$340^{o}K$ ($100^{o}F$-$150^{o}F$)(4)

  Pressure: Close to 0.10 MPa (1 atm).

  Loading: to 10,000 ppm SO_2.

- Regeneration

  Temperature: $369^{o}K$ ($205^{o}F$)(9)

  Pressure: 0.068 MPa (10 psia)(9)

TABLE D-12. WELLMAN-LORD PROCESS DESCRIPTION AND EQUIPMENT (SEE FIGURE D-9)

Processing Steps	Description	Equipment Used
Flue gas pretreatment	Removal of residual fly ash by scrubbing; gas is also cooled and saturated.	Low pressure-drop (10-15 cm H_2O) venturi scrubbers, followed by an entrainment separator.
SO_2 absorption	Absorption of SO_2 in a concentrated solution of sodium sulfite and bisulfite; sodium sulfite reacts with SO_2 to form more sodium bisulfite; side reactions include oxidation of sodium sulfite forming non-regenerable sodium sulfate.	Conventional multi-stage (commonly 3 to 5 stage) (e.g., tray tower). The largest absorption unit will handle the flue gas from 150-200 MW boilers. A large capacity surge tank installed between the absorber and the regenerator.
Absorbent regeneration	Thermal treatment to release the absorbed SO_2 (some crystalling sodium sulfite precipitates out during treatment); the SO_2-bearing stream is partially condensed to remove water (which is recycled to the dissolution tank); the concentrated SO_2-bearing stream can be processed to produce elemental sulfur, sulfuric acid, or liquid SO_2. Soda ash or caustic soda is added to the dissolution tank as the make-up chemical.	Forced-circulation evaporator/crystallizer of either single-or-multiple-effect design; single-effects usually used for systems smaller than 150 MW. Stainless steel piping also recommended for all 5.1 cm (2 in.) and smaller pipes in solution service.
Purge treatment	Purging of nonreactive/nonregenerable sodium species (sulfate, thiosulfate) from the system. A slip stream is treated and a crystalline product containing primarily sodium sulfate is produced. Details of the operation are not known.	Not known.

2.5 Process Efficiency and Reliability - SO_2 removal efficiency has been proven at >90% for SO_2 concentrations up to 20,000 ppm(9). Reliability in terms of on-stream time has been >97% for all installations(4,9).

The system successfully fulfilled performance acceptance test requirements at NIPSCO, a coal-fired utility, on Sept. 15, 1977. SO_2 removal was 91%, particulate emissions were 0.072 $g/10^6$ cal (0.04 $lb/10^6$ Btu), sulfur product purity was 99.9% and sodium carbonate makeup was 0.26 kg/kg sulfur removal(2).*

2.6 Raw Materials Requirements

Basis - Performance of oil-fired systems in Japan using Wellman-Lord process.

Sodium makeup: 5%-20% of absorbed sulfur value. A purge containing 10% of the absorbed sulfur value tied up as sodium salts corresponds to a sodium makeup equivalent to 0.25 kg NaOH or 0.33 kg Na_2CO_3 per kg S absorbed(4).

Basis - NIPSCO coal-fired boiler acceptance test results.

Sodium carbonate: equivalent to 9.4% of SO_2 absorbed.

2.7 Utility Requirements

Steam: 15 kg/kg SO_2absorbed(9).† Another source reports 5-10 kg steam/kg SO_2 evaporated(6). 25,455-29,318 kg/hr (56,000-64,500 lb/hr) usage reported for NIPSCO system(1). This is equivalent to 14.5-16.5 kg steam/kg SO_2 absorbed.

Electricity: 3.0 $kcal/Nm^3$ flue gas (0.0056 kw/scfm)(9)

Process Water: 0.055 l/Nm^3 flue gas (0.0004 gal/scf) including prescrubber(9).

Electricity: 3.72 $kcal/Nm^3$ (0.0070 kw/scfm)(4).

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*Calculated from data reported for NIPSCO acceptance tests performance.

†Calculated from data in Reference 2 based on acceptance test data at NIPSCO plant.

Cooling Water: 1.1 liters/Nm^3 (0.008 gal/scf)(9).

Reheater Flue Gas, 1010 Btu/scf (9000 kcal/m^3): 215 Nm^3/hr (7600 scf/hr) based on 100 tonne per day Claus plant for reheat to 588°K (600°F).

3.0 Process Advantages

- A concentrated SO_2 stream containing up to 90% SO_2 can be produced(4).
- Can remove in excess of 95% of SO_2 from streams containing as much as 20,000 ppm(9).
- By installing large surge capacity, absorption and regeneration sections of plant can operate independently, thus enhancing its reliability(4).
- Low scale potential in the scrubber system; no potential of calcium scaling(4).
- Ability to separate the scrubber system operation from the regeneration section, which allows the use of a centrally located regeneration facility serving a number of different scrubbers(4).
- Considerable operating experience has been obtained with oil-fired boilers, sulfuric acid plants, and Claus plants in addition to the present coal-fired utility at NIPSCO(7).
- The sulfuric acid plant size requirements are relatively small due to the high concentration of recovered SO_2(7).
- Low liquid-to-gas ratios are required in the scrubber(7).

4.0 Process Limitations

- Sensitivity of the system operation to the buildup of contaminants. The system requires a prescrubber for feed gases containing high particulate loading. The liquid bleed from the prescrubber has a low pH (1.5-2.0) and must be neutralized prior to being discharged(4).
- Some oxidation of sulfite to nonreactive sulfate if high sulfur trioxide or high oxygen levels exist in the feed gas(4).
- Small quantities of nonreactive sodium species such as sodium sulfate, thiosulfate, (formed from H_2S, COS, CS_2 in gas) must be purged from the system and replaced by caustic or soda ash. This creates a handling and disposal problem(4).

- The process operates near the solubility limit of sodium sulfite in designs where a prescrubber is not needed. If the SO_2 level in the feed gas drops suddenly, less of the more soluble sodium bisulfite would be formed and sodium sulfite precipitation could occur locally in the scrubber as the gas is cooled(4).
- High steam usage: around 6-10 kg steam per kg SO_2 absorbed(6,9), depending on the application.
- The evaporator system must be maintained free of solids(7).
- Problems have arisen in the past from pitting corrosion of evaporation tubes(7).

5.0 Process Economics(9)

A Wellman-Lord unit handling a gas containing 5820 kg/hr (12,800 lbs/hr) SO_2 is estimated to cost about 16 million dollars (1978). A unit handling 580 kg/hr (1200 lbs/hr) SO_2 is estimated to cost about 2.3 million dollars (1978). These estimates do not include facilities for incineration or SO_2 compression.

6.0 Input Streams

6.1 Raw gas (Stream 1): See Table D-13.

6.2 Steam (Stream 3): 0.3 MPa saturated (30 psia)

6.3 Soda ash or caustic (Stream 4); 3.7 tonnes/day for a 100 tonne/day Claus plant(8)

6.4 Venturi makeup water (Stream 2): Not required for Claus plant, can use cooling water; no operating data available.

6.5 Cooling water (Stream 7): No operating data available, designs usually specify a 14^{o}K (25^{o}F) temperature rise.

6.6 Makeup water (Stream 11): No data available.

7.0 Discharge Streams

7.1 Reheater Exhaust Gas (Stream 5) - See Table D-13.

7.2 Concentrated SO_2 Stream (Stream 10)(8) - 85 vol % SO_2, 15% H_2O.

7.3 Pretreatment Scrubber Blowdown (Stream 6) - No data available.

TABLE D-13. TYPICAL COMPOSITION OF GAS STREAMS ENTERING AND LEAVING 100 TONNE PER DAY REFINERY CLAUS PLANT WITH WELLMAN-LORD TAIL GAS PROCESS(8)

Composition (Vol %)	Claus Incinerated Exhaust	Quench Outlet (Absorber Inlet) Stream 1	Absorber Outlet Stream 8	Reheater Exhaust to Atmosphere Stream 15
SO_2	1.08	1.34	250 ppm	215 ppm
CO_2	4.23	5.26	5.33	5.66
H_2O	26.57	8.76	8.88	9.80
N_2	66.68	82.85	83.98	82.43
O_2	1.44	1.79	1.81	2.11
Temperature	650°C	43°C	43°C	316°C
Pressure	0.1 MPa (14.7 psia)	0.1 MPa (14.7 psia)	0.1 MPa (14.7 psia)	0.1 MPa (14.7 psia)

TABLE D-14. APPROXIMATE COMPOSITION OF WELLMAN-LORD PURGE STREAM FROM CLAUS PLANT APPLICATION(8,9)*

Component	Wt %
TDS:	26
Na_2SO_4	5
$Na_2S_2O_5$	7
Na_2SO_3	14
$Na_2S_2O_3$	†
Water	74

*No centrifuge in the system; water added to dissolve all solids.

†Actual amount in solution unknown, but is estimated to be about 1% by weight.

7.4 Purge Stream (Stream 8) - See Table D-14 for Claus plant application, composition for fossil fuel boiler will be different.

7.5 Heat Exchanger Condensate (Stream 9) - No data available.

8.0 Data Gaps and Limitations

Several limitations exist in Wellman-Lord process operating data; these include:

- Lack of stream characterizations for most streams due to the proprietary nature of the process.
- Actual operating data are limited for commercial installations.
- Data are lacking on the most optimized version of the process which would operate with double-effect evaporators, and convert purged salts to a final, solid by-product or waste material.

9.0 Related Programs

EPA has contracted for an independent analysis of the full-scale Wellman-Lord process at NIPSCO. The objectives of the test program are to: assess the technical and economic feasibility of the process; determine the applicability and control capability of the process; determine the magnitude and characteristics of the liquid and solid waste streams; and investigate performance with respect to varying inlet flue gas conditions. An interim report on the testing/analytical results is expected to be published in late 1978 or early 1979.

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9. Information provided to TRW by L. H. Grieves of Davy Powergas, June 16, 1978.

CHIYODA THOROUGHBRED 101 PROCESS

1.0 General Information

1.1 Operating Principles(1,2,3) - Purification of boiler flue gas or incinerated Claus tail gas, utilizing a dilute sulfuric acid solution with a catalyst to absorb/oxidize SO_2. Gypsum is produced as an end product. The scrubbing liquor used to absorb SO_2 is sent to an oxidizer where residual sulfurous acid is oxidized to sulfuric acid. Sulfuric acid from the oxidizer is neutralized with limestone to crystallize and separate gypsum. The absorber offgas is reheated and discharged to the atmosphere.

1.2 Developmental Status(4) - Commercially available and fully tested both in the U.S. and Japan. A new process modification that will remove oxides of nitrogen has been piloted(6).

1.3 Licensor/Developer - Chiyoda Chemical Engineering and Construction Co., Ltd.

Chiyoda International Corp.
1300 Park Place Building
1200 6th Avenue
Seattle, Washington 98101
(206) 624-9350

1.4 Commercial Applications(1) - The Chiyoda Thoroughbred 101 process has been applied to three Claus sulfur plants, eight industrial boilers and one industrial incinerator in Japan, as of mid-1974(1). In the U. S., Chiyoda International has tested a 23-MW prototype unit on a coal fired utility boiler at Plant Scholz Station of Gulf Power Co. in Sneads, Florida(5). Presently, there are fifteen Chiyoda installations in Japan(4).

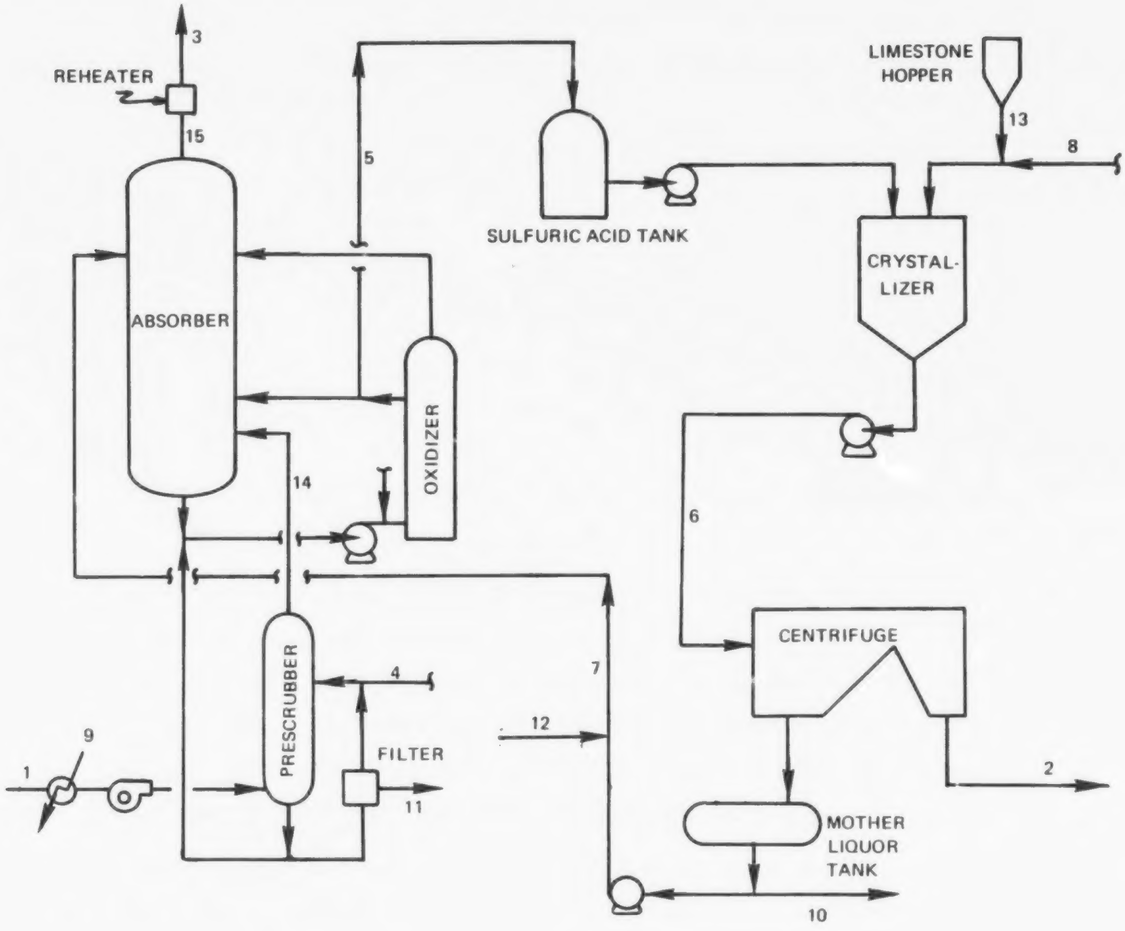
2.0 Process Information

2.1 Simplified Flow Diagram (see Figure D-10)(1,2,3) - Incinerated Claus flue gas (Stream 1) is scrubbed with recirculated water for removal of particulate matter and cooling to approximately 328^{o}K (131^{o}F). Particulates scrubbed from the flue gas are filtered from the scrubbing water before returned to the prescrubber. The SO_2 contained in the flue gas is absorbed by dilute (2%-3%) sulfuric acid in the absorber at 323^{o}K to 343^{o}K (120^{o}F to 160^{o}F). Absorber vent gas is reheated by direct combustion of fuel to avoid steam plume formation from the stack. Sulfurous acid formed in the absorber is reacted with oxygen from the air in the oxidizer to produce sulfuric acid in the presence of soluble sulfate catalyst. Sulfuric acid produced in the oxidizer (Stream 5) is neutralized with limestone, or other calcium compound, in the crystallizer, thus producing gypsum. Gypsum crystals are separated by a centrifuge and dry gypsum (5% to 20% moisture content) is conveyed to storage (Stream 2). Catalyst makeup is added to the mother liquor tank before the liquor is recycled to the absorber (Stream 7). Some purging (Stream 10) of liquor may be required to minimize the level of solubles in the system. The purge rate is determined by the rate at which solubles enter the system via flue gas particulate matter or corrosion.

2.2 Equipment - Venturi prescrubber, stainless steel absorber (packed column), Chevron type mist eliminator, oil or gas fired reheater, bubbling column oxidizer. Dilute sulfuric acid storage tank, limestone silo and slurry vessel, precipitator/crystallizer reactor clarifier; centrifuge and fly ash thickener.

2.3 Feed Stream Requirements(5,6)

- Pressure: No experience above one atmosphere.
- Temperature (Flue Gas): typically 427^{o}K-478^{o}K (310^{o}F-400^{o}F), no actual restriction.


3
REHEATER
15
5
SULFURIC ACID TANK
LIMESTONE HOPPER
13
8
CRYSTAL-LIZER
ABSORBER
OXIDIZER
14
6
CENTRIFUGE
PRESCRUBBER
4
7
12
9
1
FILTER
11
2
MOTHER LIQUOR TANK
10

LEGEND:

1. INCINERATED CLAUS TAIL GAS, SO_x RICH
2. GYPSUM TO STORAGE
3. VENT GAS
4. PRESCRUBBER MAKEUP WATER
5. SULFURIC ACID RICH SOLUTION
6. NEUTRALIZED SOLUTION
7. MOTHER LIQUOR
8. AIR
9. STEAM
10. MOTHER LIQUOR PURGE STREAM
11. FILTER SOLIDS
12. CATALYST SOLUTION
13. CALCIUM SALT
14. PRESCRUBBER OFFGAS
15. S
15. ABSORBER OFFGAS

Figure D-10. Chiyoda Process

- Loading: Normally designed for about 2000 ppm SO_2 inlet concentration, but can be designed for any typical utility flue gas concentrations resulting from coal combustion. Maximum loading to date is 11,000 ppm SO_2.
- Other: Absorbent chloride concentrations shall not exceed 200 ppm to prevent pitting and corrosion in the stainless steel vessels.

2.4 Operating Parameters(5)

- Absorption System
  - Temperature: 322^oK (120^oF) - Normal recirculating liquid stream temperature.
  - Pressure: Atmospheric
  - Sulfuric Acid Concentration: Maintained at about 2% by weight.
- Particulate Loading: Inlet 0.2 g/Nm^3 (0.1 gr/scf)
  Outlet 0.02 g/Nm^3 (0.01 gr/scf)

2.5 Process Efficiency and Reliability(1,6)

- Process efficiency is dependent upon liquid-to-gas ratio used in the absorber, which in turn determines the absorber packing height. Typical process efficiency is about 95%, but efficiencies of over 99% have been achieved. The capability for removing H_2S, COS, CS_2, HCN and other possible species from coal gasification is not known.

Some problems which have occurred at the Gulf demonstration facility required minor process redesign. Several plants are operating in Japan with greater than 99% reliability(8).

2.6 Raw Material Requirements

- Catalyst: ferric sulfate solution can be any value up to saturation(8)
- Calcium Salt: 21.1 tonne/day (23.3 ton/day) based on use at limestone (90% purity) for a 100 tonne/day Claus plant.
- Air: Quantity not known.

2.7 Utility Requirements(1) - (Based on 100 tonne per day Claus plant).

- Electricity: 425 kwh/hr
- Fuel gas (9,000 kcal/m^3, 1012 Btu/scf)
  (4,256 Nm^3/min. 158,750 scfm)
- Cooling water (5.6°K, 10°F Rise): 64.5 l/sec (1020 gpm)
- Steam (3.2 MPa, 470 psia saturated): 2470 kg/hr (5446 lb/hr)

3.0 Process Advantages

- Continuous Stable Operation - No slurry is used in the absorption and oxidation processes, thereby avoiding any scaling or clogging problems(2).
- Special chemicals and utilities are not required(2).
- Gypsum produced is of sufficiently good quality for use in wallboard(1). Gypsum shows good mechanical stability, not requiring stabilization for landfilling.
- Simple process flow results in operational flexibility and lower construction/operation cost(2,3).

4.0 Process Limitations

- If the gypsum produced is not marketable, it must be transported to a landfill(1).
- Process offgas may have to be reheated before discharging into the atmosphere depending on stack requirements(1,2).
- Relatively large packed absorber size required.
- Chloride levels in the absorbent solution must be controlled below 200 ppm.
- Since the process requires the handling of sulfuric acid solutions, special corrosion resistant metals are required(7).
- Special corrosion resistant alloys are required (e.g., 316 LS.S for linings(8).

5.0 Process Economics(2) - (1972 dollars, Japanese yen basis*)

The following costs are based on a Chiyoda process applied to a boiler, utilizing 2.7% sulfur fuel oil.

Design conditions:

Power generating capacity, MW	250	800
Flue gas volume, Nm^3/hr (scfm)	750,000 (441,400)	2,400,000 (1,413,000)
SO_2 in flue gas, ppm	1500	1500
Flue gas temperature, °K(°F)	413 (284)	413 (284)
Desulfurization rate, %	90+	90+

Economics:

Capital investment	$4,970,000	$11,850,000
Annual fixed cost (18% of capital)	$ 894,600	$ 2,133,000
Annual operating and maintenance	$1,810,600	$ 4,779,800
Overhead (12% of O & M)	$ 109,900	$ 317,600

6.0 Input Streams

- Catalyst (Stream 12): See Section 2.6
- Calcium salt (Stream 13): See Section 2.6
- Make-up Water (Stream 4): See Section 2.6

7.0 Intermediate Streams(1)

- SO_x rich gas (Stream 1): see Table D-15
- Prescrubber offgas (Stream 14), see Table D-15
- Absorber offgas (Stream 15), see Table D-15

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*Chiyoda personnel feel that these dollar figures are low, partially due to low conversion rates in 1972(8).

TABLE D-15. TYPICAL CHIYODA PROCESS GAS STREAM COMPOSITIONS*(1)

Components (Vol %)	Incinerated Claus Tail Gas (Stream 1)	Prescrubber Offgas (Stream 14)	Absorber Offgas (Stream 15)	Reheater Vent Gas (Stream 3)
SO_2	1.08	1.242	0.10†	0.0865
CO_2	4.23	4.872	4.928	5.31
H_2O	26.57	15.404	15.582	15.571
N_2	66.68	76.822	77.822	77.061
O_2	1.44	1.66	1.679	1.972
Temperature	650°C (1200°F)	55°C (131°F)	55°C (131°F)	316°C (600°F)
Pressure	0.1 MPa 14.7 Psia)	0.1 MPa (14.7 Psia)	0.1 MPa (14.7 Psia)	0.1 MPa (14.7 Psia)

*Based on a 100-tonne per day Claus plant.
†SO_2 levels below 100 ppm can be achieved in coal fired boiler application(5).

8.0 Waste Streams(1)

- Mother liquor purge stream (Stream 10) - Claus tail gas (containing about 33% water) is cooled, thereby condensing water, which must be removed from the system. For a 100 tonne per day Claus unit, 0.148 l/sec (2.34 gpm) is purged with the following composition (in weight percent):

H_2O	97.0%
H_2SO_4	0.8%
MgO	2.2%
$Fe_2(SO_4)_3$ (catalyst)	trace

- Gypsum - (Stream 2) - moisture content of 5 to 20 percent. Gypsum quality is dependent upon the impurities in the limestone feed.
- Reheater Vent gas (Stream 3) see Table D-15.
- Filtered solids (Stream 11) composition dependent on the characteristics of the input gas.

9.0 Data Gaps and Limitations

- Cost data for Claus plant application are not available.
- Quantity of catalyst required is not known.
- Detailed characterization data not available for all input, intermediate and waste streams.

10.0 Related Studies: Not known.

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SHELL COPPER OXIDE PROCESS

1.0 General Information

1.1 Operating Principles - A concentrated SO_2 gas stream is produced by reaction ("adsorption") of sulfur oxides with CuO, followed by in-situ regeneration using a reducing gas at approximately the same temperature as SO_2 adsorption. The concentrated SO_2 stream is sent to a Claus plant for sulfur recovery.

1.2 Development Status - Commercially available for oil refineries. Pilot plant testing in coal-burning power plant.

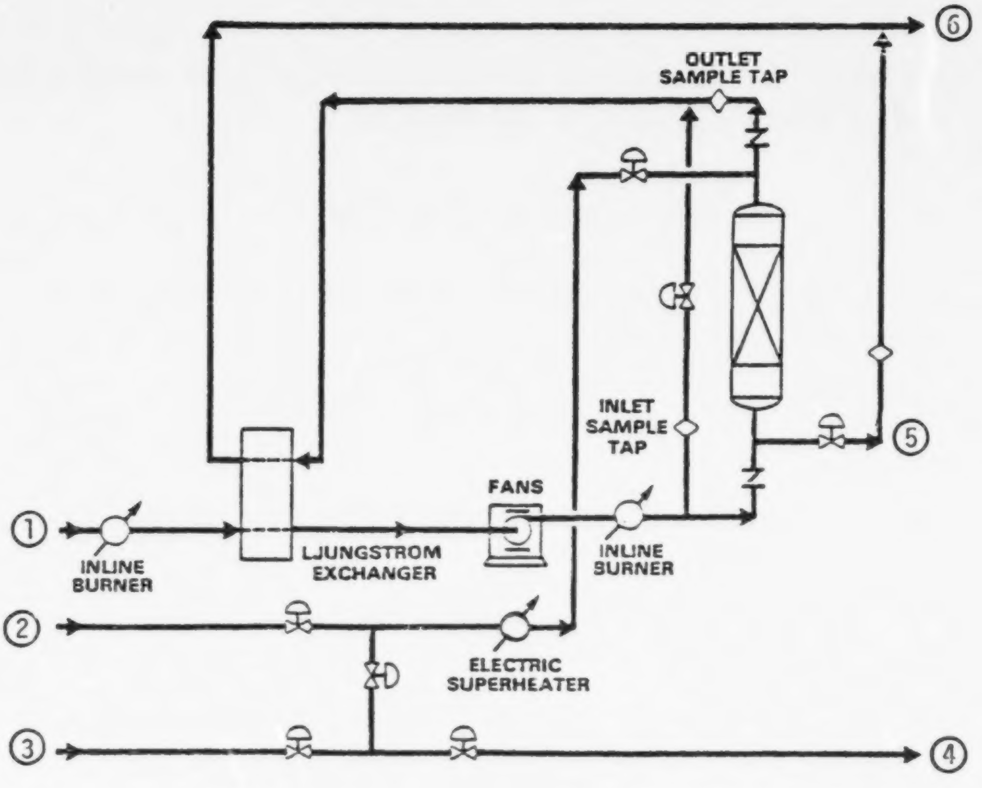
1.3 Licensor/Developer - Developed by Shell International Petroleum, The Hauge, Netherlands. Licensor:

Universal Oil Products Company
Des Plains, Ill.

1.4 Commercial Applications(1,2) - One unit is currently in operation at the Showa Yokkaichi Sekiyu in Japan, with a capacity of 2.8×10^6 Nm^3/D (103 MMSCFD). The pilot plant at Tampa Electric Company's (TECO) Big Bend Station has a capacity of 55.6×10^3 Nm^3/D (2.0 MMSCFD).

2.0 Process Information

2.1 Flow Diagram Pilot Plant(2) (see Figure D-11) - A raw gas stream is heated to about 644^oK (700^oF) by heat exchange with the treated gas followed by a trim burner for temperature control. The gas enters the fixed-bed reactor containing CuO on alumina where it is "adsorbed"


⑥
OUTLET SAMPLE TAP
INLET SAMPLE TAP
⑤
FANS
①
INLINE BURNER
LJUNGSTROM EXCHANGER
INLINE BURNER
②
ELECTRIC SUPERHEATER
③
④

LEGEND:

1. Flue Gas
2. Steam
3. Hydrogen
4. Hydrogen Vent
5. Product Gas
6. Regeneration Off-gas

Figure D-11. Shell Flue Gas Desulfurization Process for TECO Pilot Plant(2) on the dry bed. The principal reaction between SO_2 in the flue gas and copper activated alumina absorbent is:

$$SO_2 + 1/2\ O_2 + CuO \rightarrow CuSO_4$$

The bulk of the accepted sulfur is released during the regeneration cycle. Hydrogen is used for regeneration:

$$CuSO_4 + 2H_2 \rightarrow Cu + SO_2 + 2H_2O$$

During the initial stages of adsorption, the Cu produced during regeneration is oxidized:

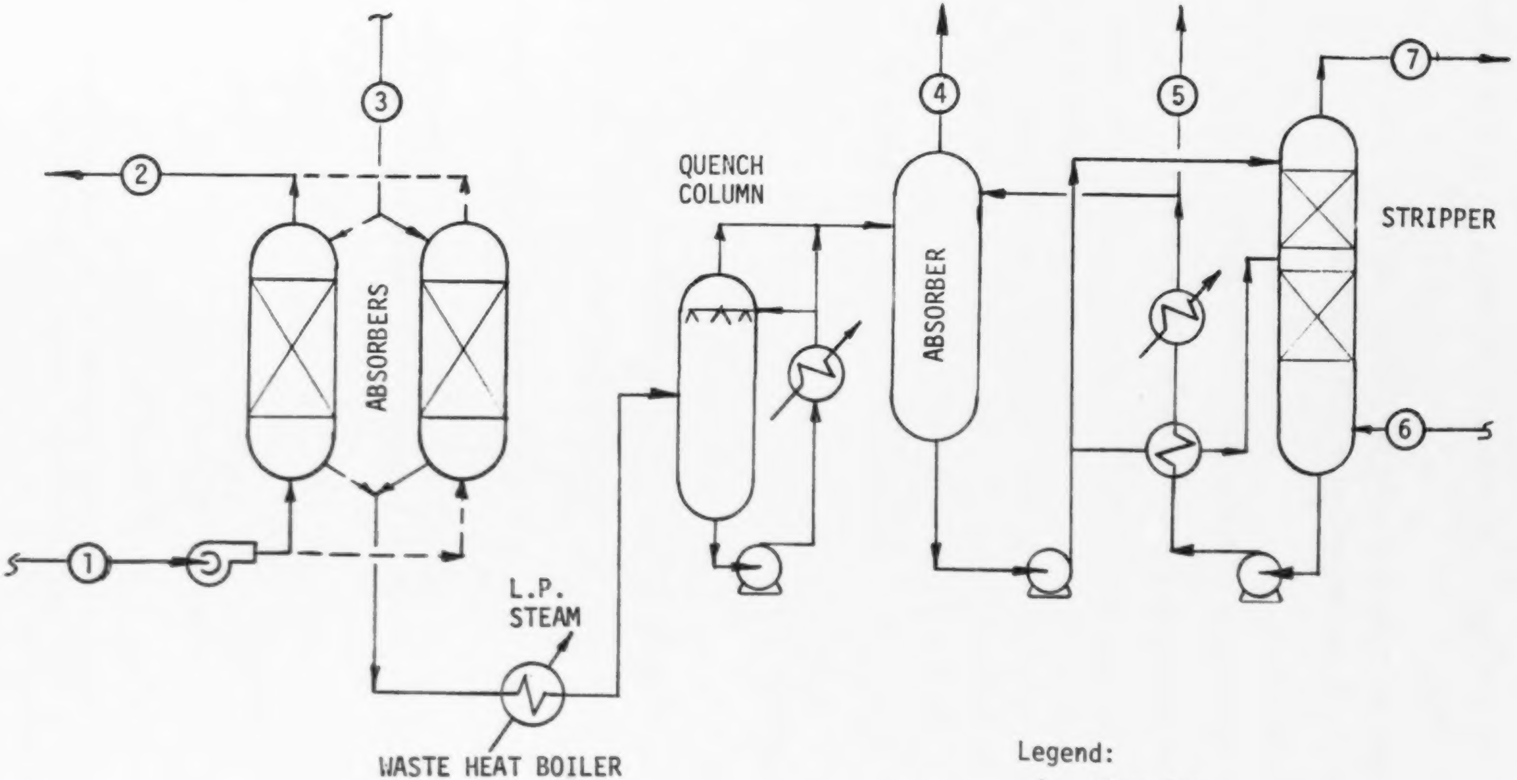
$$Cu + 1/2\ O_2 \rightarrow CuO$$

Any Cu_2S present in the regenerated acceptor is oxidized:

$$Cu_2S + 2\ 1/2O_2 \rightarrow CuO + CuSO_4$$

During regeneration the reactor is isolated from flue gas by flapper valves and the gas flow is bypassed. Both treated gas and regenerated gas are sent to the stack.

2.2 Flow Diagram - Yokkaichi Plant(9) (see Figure D-12) - Flue gas from an oil-fired boiler at 673^oK (752^oF) containing 1300 ppm SO_2 flows into one of the two adsorber reactors. Approximately 90% of the SO_2 is absorbed as described in Section 2.1. After 90 minutes, the flue gas is introduced into the second absorber, while the first absorber is regenerated. The two adsorbers are alternated between the acceptor and regeneration stages to allow continuous operation. Because the SO_2 released from regeneration will vary from nil to a maximum every 90 minutes, an absorber-stripper system is utilized to produce a constant flow to the Claus plant. About 99.5% of the SO_2 is absorbed (in water, under pressure) and then removed from the absorber liquor in the stripper column.



3
2
QUENCH COLUMN
4
5
7
STRIPPER
ABSORBERS
ABSORBER
6
1
L.P. STEAM
WASTE HEAT BOILER

Legend:

1. Flue Gas
2. Treated Flue Gas
3. Regeneration Gas (Hydrogen)
4. Absorber Offgas
5. Excess Stripper Water
6. Low Pressure Steam
7. SO_2 to Claus Plant

Figure D-12. Shell CuO Process (Yokkaichi Plant)(9)

2.3 By-Product - SO_2 rich gas. In a commercial plant, SO_2 can be reduced to elemental sulfur.

2.4 Equipment - Reactor fixed bed adsorber. Flue gas flows through open channels alongside the acceptor. Designed by UOP.

2.5 Operating Parameters

- Adsorption temperature: 644°K-700°K (700°F-800°F)
- Regeneration temperature: 644°K-700°K (700°F-800°F)

2.6 Process Efficiency and Reliability(1): 90% SO_2 removal efficiency. No data for process reliability. The Yokkaichi plant experienced the following operational problems: quench column corrosion, sticking of the hydrogen line valve and plugging of waste heat boiler tubes. These problems have been solved.

2.7 Raw Material Requirements - Hydrogen(9): 0.19 to 0.20 kg/kg of S recovered.

2.8 Utility Requirements - ?

3.0 Process Advantages

- Dry process - handling of waste slurries not required.
- Acceptance and regeneration occur at the same temperature obviating any heating or cooling of adsorption beds.
- Continuous processing can be achieved by using two units in alternating acceptor and regenerator modes.
- Process could be expanded for NO_x removal by ammonia injection into acceptor bed. CuO and $CuSO_4$ as catalysts for reduction of NO_x to nitrogen gas.

4.0 Disadvantages

- Equipment costs are high.
- A hydrogen source is needed for regeneration.
- Stripper requires steam, i.e., high energy inputs.
- The steam used in regeneration results in an acidic wastewater stream. (In the pilot plant, the steam is vented to the stack with the regeneration off-gas.)

5.0 Process Economics

Capital cost of the Yokkaichi plant was \$3.3 million (1974 dollars), excluding the hydrogen plant(9).

6.0 Input Streams

- Flue Gas - Yokkaichi plant(9): 673°K (752°F), 1300 ppm SO_2.

7.0 Intermediate Streams

No data reported.

8.0 Discharge Streams

- Excess Stripper Water(9): Contains 20 to 40 ppm (wt) of sulfur.
- Treated Flue Gas: 130 ppm SO_2 (based on 90% adsorption efficiency).

9.0 Data Gaps and Limitations

Comprehensive data are not published for either the pilot plant or commercial facility.

10.0 Related Programs

None.

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LIME/LIMESTONE SLURRY SCRUBBING PROCESSES

1.0 General Information

1.1 Operating Principles - Sulfur dioxide absorption in a lime or limestone slurry. The spent slurry is discharged to a settling pond or thickener with the return of the clarified liquid to the scrubber circuit.

1.2 Developmental Status - Commercially available.

1.3 Licensors/Developers(1,13) - The engineering design of slurry scrubbing systems for commercial installations is offered by a number of companies including Babcock and Wilcox, Chemico, Combustion Engineering, Peabody Engineering, Research Cottrell, Universal Oil Products, and Zurn Air Systems.

1.4 Commercial Applications(1) - There are currently 37 flue gas desulfurization (FGD) units (7,441 MW total capacity) operating in the United States on utility and industrial boilers, with lime or limestone scrubbing systems accounting for 82% of total operating capacity. When units currently under construction or in the planning stage are added to the present capacity, a total capacity of 50,419 megawatts (131 units) is projected of which 64% (by MW capacity) will utilize lime or limestone slurries. In Japan there are 333 operational FGD installations, 64 of which are lime/limestone systems.

With the exceptions of the few applications to tail gases from sulfuric acid and Claus plants, all existing slurry scrubbing systems in the U.S. are applied to boiler gas streams. Although no application to coal gasification currently exists, possible applications in a commercial gasification plant may be in connection with support operations such as utility boiler and sulfur recovery.

2.0 Process Information

2.1 Flow Diagram (see Figure D-13)

- Process Description(2,14) - The raw gas is treated in a venturi scrubber for the removal of residual particulates and some SO_2 (up to 30%). Additional particulates and the bulk of the remaining SO_2 are removed in an absorption tower where a slurry of lime or limestone (generally 6%-15%) is circulated. The integrated scrubber/process absorber shown can achieve up to 95% SO_2 removal. The slurry effluents from the venturi scrubber and absorber are channeled into separate "reaction tanks" where the process reactions are allowed to approach equilibrium. The overall reactions are:

(a) with lime: $Ca(OH)_2 + SO_2 \rightleftharpoons CaSO_3 \cdot 1/2\ H_2O + 1/2\ H_2O$

$$CaSO_3 + 1/2\ O_2 \rightleftharpoons CaSO_4$$

(b) with limestone: $CaCO_3 + SO_2 + 1/2\ H_2O \rightleftharpoons CaSO_3 \cdot 1/2\ H_2O + CO_2$

$$CaSO_3 + 1/2\ O_2 \rightleftharpoons CaSO_4$$

Most of the reaction tank slurries (containing precipitated reaction products) are recirculated to the scrubber and absorber. A slurry bleed stream is sent to a thickener for processing and disposal. The process may also be designed to route the slurry bleed stream directly to a disposal pond.

Residual particulate removal can be achieved by utilizing a high efficiency electrostatic precipitator or wet scrubber upstream of the absorption tower.

2.2 Equipment - Conventional absorption towers (usually spray packed towers), marble bed absorbers, venturi scrubbers, turbulent bed absorber, stirred reaction tanks, and thickeners.

In addition to conventional absorbers, a number of newly developed variations are now in service, such as the venturi rod scrubber, and eggcrate (polygrid packed absorber) scrubber.

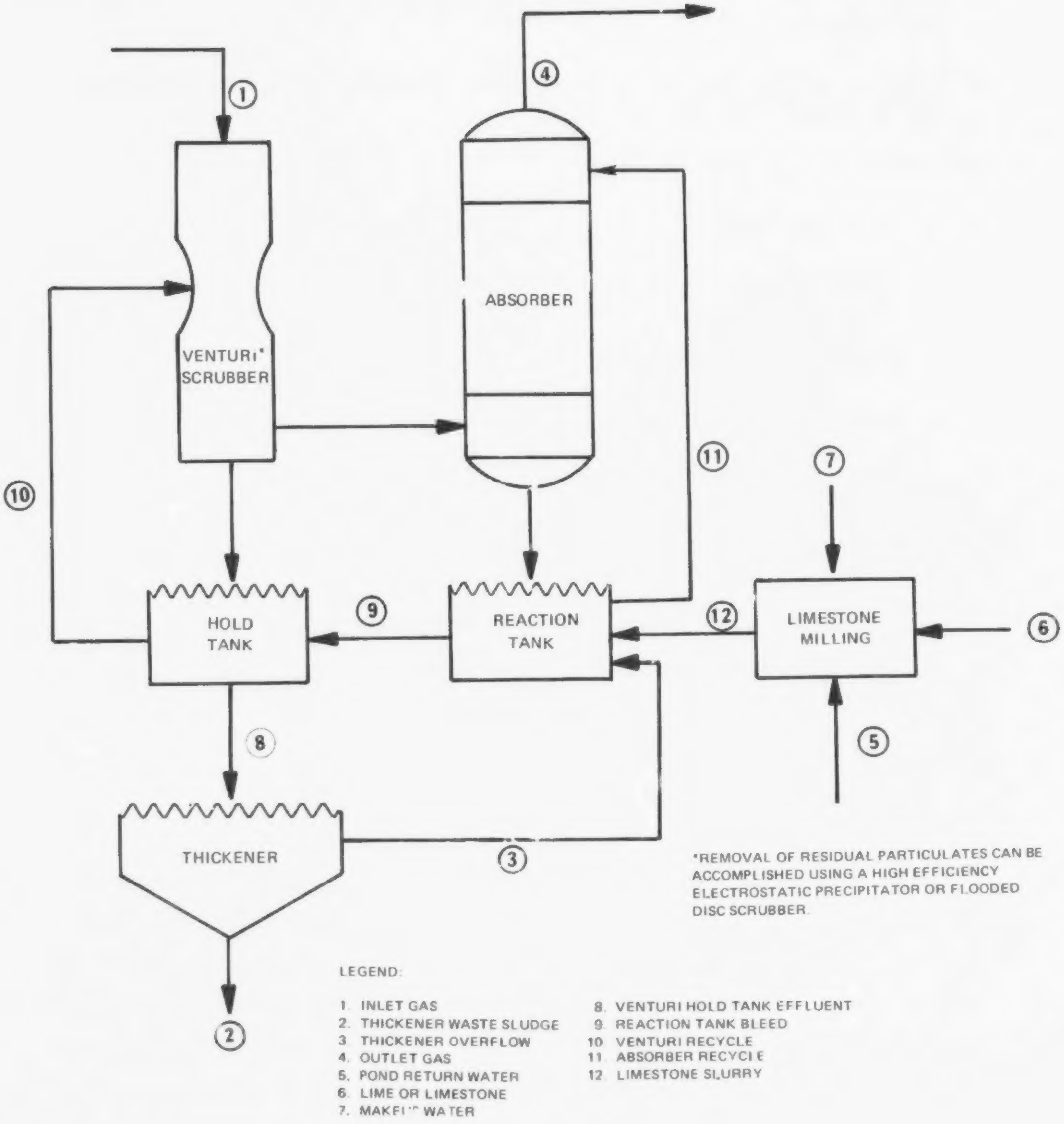
①
④
VENTURI*
SCRUBBER
ABSORBER
⑩
⑪
⑦
HOLD
TANK
⑨
REACTION
TANK
⑫
LIMESTONE
MILLING
⑥
⑧
⑤
THICKENER
③
②
*REMOVAL OF RESIDUAL PARTICULATES CAN BE ACCOMPLISHED USING A HIGH EFFICIENCY ELECTROSTATIC PRECIPITATOR OR FLOODED DISC SCRUBBER.
LEGEND:
1. INLET GAS
2. THICKENER WASTE SLUDGE
3. THICKENER OVERFLOW
4. OUTLET GAS
5. POND RETURN WATER
6. LIME OR LIMESTONE
7. MAKEUP WATER
8. VENTURI HOLD TANK EFFLUENT
9. REACTION TANK BLEED
10. VENTURI RECYCLE
11. ABSORBER RECYCLE
12. LIMESTONE SLURRY

Figure D-13. Wet lime/limestone process(2)

2.3 Feed Stream/Requirements(3)

- Temperature: $408^{o}K$ to $443^{o}K$ ($274^{o}F$-$338^{o}F$) typically
- Pressure: atmospheric
- Loading: 400 to 5000 ppm SO_2; 0.01-9.2 g/Nm^3 (0.0041-4.0 gr/scf) particulates(14)
- Other: system design favors gases produced from low chloride coals (when coal is burned).

2.4 Operating Parameters(3,14)

- Venturi Scribber
  - Temperature: flue gas temperature in venturi section, flue gas saturation temperature in the separation section
  - Pressure: atmospheric
  - Pressure drop: 30-230 mm H_2O (1.2-9.1 in. H_2O)
  - Solution circulation rate: 2-10 liters/Nm^3 (14-71 gal/1000 scf)
- Absorber(3,14)
  - Temperature: flue gas saturation temperature
  - Pressure drop: 35-505 mm H_2O (1.4-19.9 in. H_2O)
  - Solution circulation rate: 5-12 liters/Nm^3 (35.5-85 gal/1000 scf)
  - Slurry concentration: 5%-15%

2.5 Process Efficiency and Reliability - SO_2 removal efficiencies up to 95% can be expected(2), although generally efficiencies of 70%-90% are reported based on utility firing of high sulfur coal. For low sulfur coals, at least 50% of the sulfur dioxide can be removed(4). Fly ash removal efficiencies of 98% are typical for the integrated scrubbing-absorption system(5). Process reliability may be a weak point in slurry-based systems. Availabilities have been reported from 70%(5,6) up to 93% for the Kansas City Power and Light, LaCygne Unit No. 1*(13). In Japan, numbers up to 100% have been reported(3).

2.6 Raw Material Requirements

- Lime/limestone: Stoichiometries of 1.0-1.05 moles of CaO/mole SO_2 absorbed are reported in Japan(3). Limestone stoichiometries of 1.0-1.5 are required for the Kansas Power and Light installation(14).
- Fixation Agents: Patented materials are available for fixating the sludge. One such material is Calcilox by Dravo(8).
- Air(3,4,9,10,14): 350%-600% of stoichiometric quantities used in many Japanese slurry scrubbing systems to oxidize calcium sulfite sludge to gypsum by-product. Also, forced oxidation to gypsum is used increasingly in American systems to enhance solids settling, dewatering and storage properties and requires 150%-400% of stiochiometric quantities(14).
- Make-up Water: The quantity of water required for closed loop operation is determined by evaporation losses and the amount discharged with the waste sludge stream(14). 390 l/min (103 gpm) required for Kansas Power and Light installation.

2.7 Utility Requirements

- Steam: Usually none; may be used to reheat outlet flue gas.
- Fuel (for reheat): determined by flue gas flow rate and reheat required.
- Electricity(3): 1.2% to 2.1% of station power generated.
- Total Energy(3): 2%-5% of total station generation and includes pump, fan and reheat energy requirements.

2.8 Miscellaneous(3) - Scaling and corrosion problems can result from improper design and operation, and are often controlled during scheduled shutdowns to minimize unscheduled downtime.

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*Availability reflects the percentage of time when the boiler is operating and the scrubber system is available for operation. Slurry scrubbers in the U.S. generally have greater down times than utility boilers.

3.0 Process Advantages(2)

- The basic process is fairly simple and very few process steps are involved.
- The capital and operating costs are relatively low. Reserves of absorbent materials are abundant in the United States.
- SO_2 removal efficiencies are generally high.
- The two-stage treatment of flue gases allows for the removal of both SO_2 and the residual particulates.
- The lime/limestone process is the most commonly used SO_2 control method by utilities exclusive of low-sulfur fuel. Commercial installations have been operating for more than four years.

4.0 Process Limitations(2)

- Large quantities of waste sludge require processing and disposal in an environmentally acceptable manner.
- If not designed carefully or operated attentively, lime/limestone systems have a tendency towards chemical scaling, plugging, and erosion. These problems can frequently halt operation of the system.
- Oxidation of sulfite to sulfate increases the tendency towards serious scaling. Excess air, high pH, fly ash, residence time in the reaction tank, and the presence of NO_2 in the flue gas are suspected to be factors which contribute to oxidation. Scaling can be reduced by forcing the oxidation completely to gypsum.
- Efficiency of SO_2 removal decreases with decreasing sulfur content of fuel.

5.0 Process Economics

Commonwealth Edison reported the cost of the 160 MW retrofitted limestone scrubbing installation at $95/kw (1972 dollars) at its Will County (Illinois) Station. In addition, an expenditure of $13/kw is required for sludge treatment and disposal. Operating costs were estimated at 2.8 mils/1000 kcal ($0.70/MM Btu), coal fired at 60% load factor or 7.3 mils/kwh, including 2.1 mils/kwh for sludge treatment and disposal(11).

TVA updated cost estimates for lime and limestone srubbing processes designed to remove 90% of SO_2 from utility gas fired with 3.5% sulfur coal follow. On-site sludge disposal and 7,000 hrs/yr operation are assumed for new facilities. Sludge fixation costs are excluded. Cost basis: mid-1977(1).

	Capital Investment, $/ kw		
	200 MW	500 MW	1000 MW
Lime	79.9	61.1	44.9
Limestone	88.4	68.4	51.4

	Operating Costs, Mils/kwh		
	200 MW	500 MW	1000 MW
Lime	4.54	3.65	2.94
Limestone	4.20	3.41	2.74

Sludge fixation would add 15%-20% to the annual operating cost(1).

6.0 Input Streams

- Inlet gas (Stream 1) - see Table D-16.
- Lime or limestone (Stream 6) - see Section 2.6.
- Make-up water (Stream 7) - see Section 2.6.

7.0 Intermediate Streams

- Limestone slurry (Stream 12).
- Venturi hold tank bleed (Stream 8) - see Table D-17.
- Reaction tank bleed (Stream 9) - see Table D-18.
- Venturi recycle (Stream 10) - same composition as Intermediate Stream 8 - see Tables D-17 and D-19.
- Absorber recycle (Stream 11) - same composition as Intermediate Stream 9 - see Tables D-18 and D-20.

TABLE D-16. PROPERTIES OF FEED GAS TO LIME/LIMESTONE SO_2 SCRUBBERS (STREAM 1)

	Kentucky Utility Green River(7) Lime Scrubber	Kansas Power and Light Lawrence No. 4(10) Limestone Scrubber	Kansas City Power and Light La Cygne Unit No. 1(12) Limestone Scrubber
Temperature	422°K (300°F)	411°K (280°F)	411°K (280°F)
Flow Rate	611,280 m^3/hr (360,000 ACFM) 382,466 Nm^3/hr (238,000 SCFM dry)	684,294 m^3/hr (408,000 ACFM)	4,686,480 m^3/hr (2,760,000 ACFM total, 7 scrubbers)
Particulate	5.3 g/Nm^3 dry (2.2 gr/SCF dry)	7.25 g/Nm^3 dry (3 gr/SCF dry)	17.8 g/1000 kcal (9.9 lb/MM Btu)
SO_2	49.4 kg/min (108.9 lb/min)	748 ppm	5000 - 5700 ppm
H_2O	45,239 liters/min (11,968 gpm)	--	--
Particulate Ash Analysis			
P_2O_5	--	--	0.15
SiO_2	--	--	46.1
FeO	--	--	19.2
Al_2O_3	--	--	14.1
CaO	--	--	6.9
MgO	--	--	1.0
SO_3	--	--	7.9
K_2O	--	--	2.5
Na_2O	--	--	0.6
TiO	--	--	1.0
Other	--	--	0.7

TABLE D-17. VENTURI SCRUBBER SLURRY BLOWDOWN AT KANSAS POWER AND LIGHT LAWRENCE NO. 4[(10)] - LIMESTONE SCRUBBER (STREAM 8)

Parameter	Value
Flow Rate	3037 kg/hr (6695 lb/hr) 473 liter/min (125 gpm)
Solids Conc*	9-11%
Dissolved Ions*	
Ca^{++}	876 ppm
Mg^{++}	137 ppm
$SO_3^=$	106 ppm
$SO_4^=$	2,340 ppm
Solids Composition*	
$CaSO_3 \cdot 0.5\ H_2O$	2.41 wt %
$CaSO_4 \cdot 2\ H_2O$	11.57 wt %
$CaCO_3$	5.85 wt %
$CaSO_4$ Relative Saturation*†	1.45

*At 100% limestone feed stoichiometry.

†Relative saturation of 1.45 indicates a calcium sulfate supersaturation of 45% under certain conditions.

TABLE D-18. REACTION TANK BLOWDOWN AT KANSAS POWER AND LIGHT LAWRENCE NO. 4(10) - LIMESTONE SCRUBBER (STREAM 9)

Flow Rate	957 kg/hr (2110 lb/hr) 151.4 liters/min (40 gpm)
Solids Conc*	5 - 7%
Dissolved Species*	
Ca++	715 ppm
Mg++	127 ppm
$SO_3^=$	23 ppm
$SO_4^=$	2,064 ppm
Solids Composition*	
$CaSO_3 \cdot 0.5\ H_2O$	0.20 wt %
$CaSO_4 \cdot 2\ H_2O$	19.25 wt %
$CaCO_3$	21.52 wt %
$CaSO_4$ Relative Saturation*†	1.22

*At 100% limestone feed stoichiometry.

†Relative saturation of 1.22 indicates a calcium sulfate supersaturation of 22% under certain conditions.

TABLE D-19. VENTURI SCRUBBER RECYCLE LIME/LIMESTONE SCRUBBER (STREAM 10)

	Kansas Power and Light Lawrence No. 4(10) Limestone Scrubber	Kentucky Utility Green River (7) Lime Scrubber
Flow Rate *		
H_2O	--	44,663 liters/min (11,800 gpm)
$Ca(OH)_2$	--	49.4 kg/min (109 lb/min)
Ca_xSO_x	--	3348 kg/min (7,380 lb/min)
Total	13,626 liters/min (3,600 gpm)	--
Solution Circulation Rate	2.67 liters/m^2 (20 gal/1000 ACF)	--

*At 100% limestone feed stoichiometry.

TABLE D-20. ABSORBER RECYCLE LIMESTONE SCRUBBER (STREAM 11)

	Kansas Power and Light Lawrence No. 4(1) Limestone Scrubber	Northern States Power Sherburne County (4) Limestone Scrubber
Flow Rate	20,061 liters/min (5,300 gpm)	--
L/G	4.0 liters/m^3 (30 gal/1000 ACF)	--
pH	--	5 - 5.5
Dissolved Calcium	--	500-700 ppm
Dissolved Magnesium	--	1,500-2,500 ppm
Dissolved Sulfate	--	8,000-15,000 ppm
Dissolved Sulfite	--	0
Solid Calcium	--	1 - 10% (wt)
Solid Magnesium	--	0.5 - 1.5%
Solid Sulfate	--	15 - 20%
Solid Sulfite	--	0

8.0 Discharge Streams

- Thickener waste sludge (Stream 2)

  Kentucky Utility - Green River(7) Lime Scrubber

  Flow Rate

H_2O:	863 liters/min (228 gpm)
$Ca(OH)_2$:	4.1 kg/min (9.0 lb/min)
$CaSO_x$:	86.2 kg/min (190 lb/min)

- Outlet gas (Stream 4) - see Table D-21.
- Thickener overflow (Stream 3) - no data available.
- Pond return water (Stream 5) - see Table D-22.

9.0 Data Gaps and Limitations

Although numerous articles have been published describing operation of lime and limestone slurry scrubbing processes, full stream characterization data are usually unavailable for a given full-scale operating plant. Notably, gas composition data, liquid stream comprehensive trace element analysis data, flue gas reheat fuel requirements and realistic capital and operating costs are unavailable.

10.0 Related Programs

To minimize the chemical limitations of lime and limestone systems, efforts have been made to improve the process by the use of magnesium additives. Research conducted at the bench-scale and pilot plant level has stimulated further work on prototype facilities (EPA/TVA Alkali Scrubbing Test Facility, Shawnee Station), and at the demonstration level (EPA Scrubber/Sludge Evaluation Program, Paddys Run Station, Louisville Gas and Electric). Two proprietary absorbents have been developed, one by Dravo (thiosorbic lime), the other by Pullman Kellogg (catalytic limestone)(9).

TABLE D-19. VENTURI SCRUBBER RECYCLE LIME/LIMESTONE SCRUBBER (STREAM 10)

	Kansas Power and Light Lawrence No. 4(10) Limestone Scrubber	Kentucky Utility Green River (7) Lime Scrubber
Flow Rate*		
H_2O	--	44,663 liters/min (11,800 gpm)
$Ca(OH)_2$	--	49.4 kg/min (109 lb/min)
Ca_xSO_x	--	3348 kg/min (7,380 lb/min)
Total	13,626 liters/min (3,600 gpm)	--
Solution Circulation Rate	2.67 liters/m^2 (20 gal/1000 ACF)	--

***At 100% limestone feed stoichiometry.**

TABLE D-20. ABSORBER RECYCLE LIMESTONE SCRUBBER (STREAM 11)

	Kansas Power and Light Lawrence No. 4(1) Limestone Scrubber	Northern States Power Sherburne County (4) Limestone Scrubber
Flow Rate	20,061 liters/min (5,300 gpm)	--
L/G	4.0 liters/m^3 (30 gal/1000 ACF)	--
pH	--	5 - 5.5
Dissolved Calcium	--	500-700 ppm
Dissolved Magnesium	--	1,500-2,500 ppm
Dissolved Sulfate	--	8,000-15,000 ppm
Dissolved Sulfite	--	0
Solid Calcium	--	1 - 10% (wt)
Solid Magnesium	--	0.5 - 1.5%
Solid Sulfate	--	15 - 20%
Solid Sulfite	--	0

TABLE D-21. OUTLET GAS - LIME/LIMESTONE SCRUBBER (STREAM 4)

	Kentucky Utility Green River (7) Lime Scrubber	Kansas Power and Light Lawrence No. 4(10) Limestone Scrubber
Temperature	320°K (116°F)	336°K (144°F)
Flow Rate	514,494 m^3/hr (303,000 ACFM saturated) 382,466 Nm^3/hr (238,000 SCFM dry)	616,374 m^3/hr (363,000 ACFM)
Particulate	0.106 g/Nm^3 dry (0.044 gr/SCF dry)	0.053-0.094 g/Nm^3 dry (0.022-0.039 gr/SCF dry)
SO_2	9.9 kg/min (21.8 lb/min)	200 ppm
H_2O	636 liters/min (168 gpm)	--
Opacity	--	2.5 - 7.5%

TABLE D-22. POND RETURN WATER - LIMESTONE SCRUBBER (STREAM 5)

	Kansas City Power and Light La Cygne Unit No. 1(12) Limestone Scrubber
Calcium	696 ppm
Magnesium	48 ppm
Sodium	22 ppm
Potassium	23 ppm
Bicarbonate	36.6 ppm
Chloride	177.8 ppm
Sulfate	1627 ppm
Sulfite	Not detected
Silica	20.6 ppm
pH	7.0
Conductivity	4380 micromhos

Two pilot plants, sponsored by the EPA, are actively involved in forced oxidation test programs to enhance solids settling properties, to decrease sludge disposal land requirements, and to improve the quality of recycled water. They are: TVA/EPA Alkali Scrubbing Test Facility, Shawnee No. 10; and EPA/IERL pilot plant, Research Triangle Park(9).

Two major suppliers are involved in chemical fixation of scrubber wastes: The Dravo Corporation and U Conversion Systems(9).

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TABLE D-21. OUTLET GAS - LIME/LIMESTONE SCRUBBER (STREAM 4)

	Kentucky Utility Green River (7) Lime Scrubber	Kansas Power and Light Lawrence No. 4(10) Limestone Scrubber
Temperature	320^{o}K (116^{o}F)	336^{o}K (144^{o}F)
Flow Rate	514,494 m^3/hr (303,000 ACFM saturated) 382,466 Nm^3/hr (238,000 SCFM dry)	616,374 m^3/hr (363,000 ACFM)
Particulate	0.106 g/Nm^3 dry (0.044 gr/SCF dry)	0.053-0.094 g/Nm^3 dry (0.022-0.039 gr/SCF dry)
SO_2	9.9 kg/min (21.8 lb/min)	200 ppm
H_2O	636 liters/min (168 gpm)	--
Opacity	--	2.5 - 7.5%

TABLE D-22. POND RETURN WATER - LIMESTONE SCRUBBER (STREAM 5)

	Kansas City Power and Light La Cygne Unit No. 1(12) Limestone Scrubber
Calcium	696 ppm
Magnesium	48 ppm
Sodium	22 ppm
Potassium	23 ppm
Bicarbonate	36.6 ppm
Chloride	177.8 ppm
Sulfate	1627 ppm
Sulfite	Not detected
Silica	20.6 ppm
pH	7.0
Conductivity	4380 micromhos

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DUAL ALKALI PROCESS

1.0 General Information

1.1 Operating Principles - Sulfur dioxide removed by scrubbing in a liquid-vapor absorption tower using a clear, concentrated sodium sulfite absorbent solution to form sodium bisulfite. The sodium bisulfite solution is reacted with lime in a separate vessel to precipitate calcium salts and regenerate sodium sulfite which is returned to the scrubber.

1.2 Developmental Status - Commercially available although unproven on a commercial scale. Systems have been demonstrated on utility and industrial coal-fired boilers up to a maximum capacity of 32 MW in the U.S. The first full-scale application is presently under construction at Louisville Gas and Electric.

1.3 Licensor/Developer - There are various developers of the basic double alkali process, each utilizing their own patented ideas. The developers offering the most fully developed commercial processes are FMC, Envirotech and Arthur D. Little/Combustion Equipment Associates.

FMC Corporation
Environmental Equipment Division
1800 FMC Drive West
Itasca, Illinois 60143

Envirotech Corporation
Eimco BSP 669
W. 2nd South
Salt Lake City, Utah 84110

Arthur D. Little/Combustion Equipment Associates, Inc.*
555 Madison Avenue
New York, N. Y. 10022

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*Licensed under Combustion Equipment Associates.

1.4 Commercial Applications - A dilute mode, 32 MW systems was started up in March 1974 and tested by General Motors/Koch on coal-fired 6 M boilers in Parma, Ohio(1,2).

Arthur D. Little (ADL) and Combustion Equipment Associates (CEA) successfully completed testing of a 20 MW prototype at Gulf Power Company's Scholz Station in Sneads, Florida, a coal-fired facility. A concentrated mode system was started up in February 1975(3,4).

ADL/CEA presently has under construction a 277 MW demonstration system on coal-fired boilers at Louisville Gas and Electric Power Co. The system is scheduled for service in 1979(3,5).

A 250 MW system by FMC and a 575 MW system by Buell/Envirotech are in the planning stages. The FMC system is scheduled for service in 1979 at Southern Indiana Gas and Electric Co. FMC pilot plants have operated on stoker boilers, sulfuric acid plants, and on a dual-fired bark oil/coal boiler. In addition, an FMC industrial scale system has operated successfully on a chemical kiln at Modesto, California(3,6,7,8).

Full-scale utility applications of dual alkali systems ranging in size from 150 to 450 MW are in operation in Japan(9). Kureha-Kawaski, Showa Denro and Tsukishima have a number of systems operating on oil-fired boiler flue gases as listed below(2,10):

Process Supplier	Absorbent	By-Product	Number of Units
Kureha-Kawasaki	Sodium sulfite, limestone	Gypsum	3
Showa Denro-Ebara	Sodium sulfite, limestone	Gypsum	16
Tsukishing	Sodium sulfite, lime	Gypsum	4

2.0 Process Information

2.1 Flow Diagram - See Figure D-14.

- Process Description(4,7): The process consists of three major sections: absorption, regeneration and dewatering. Hot flue gas (Stream 1) enters the absorber countercurrent to a clear liquid

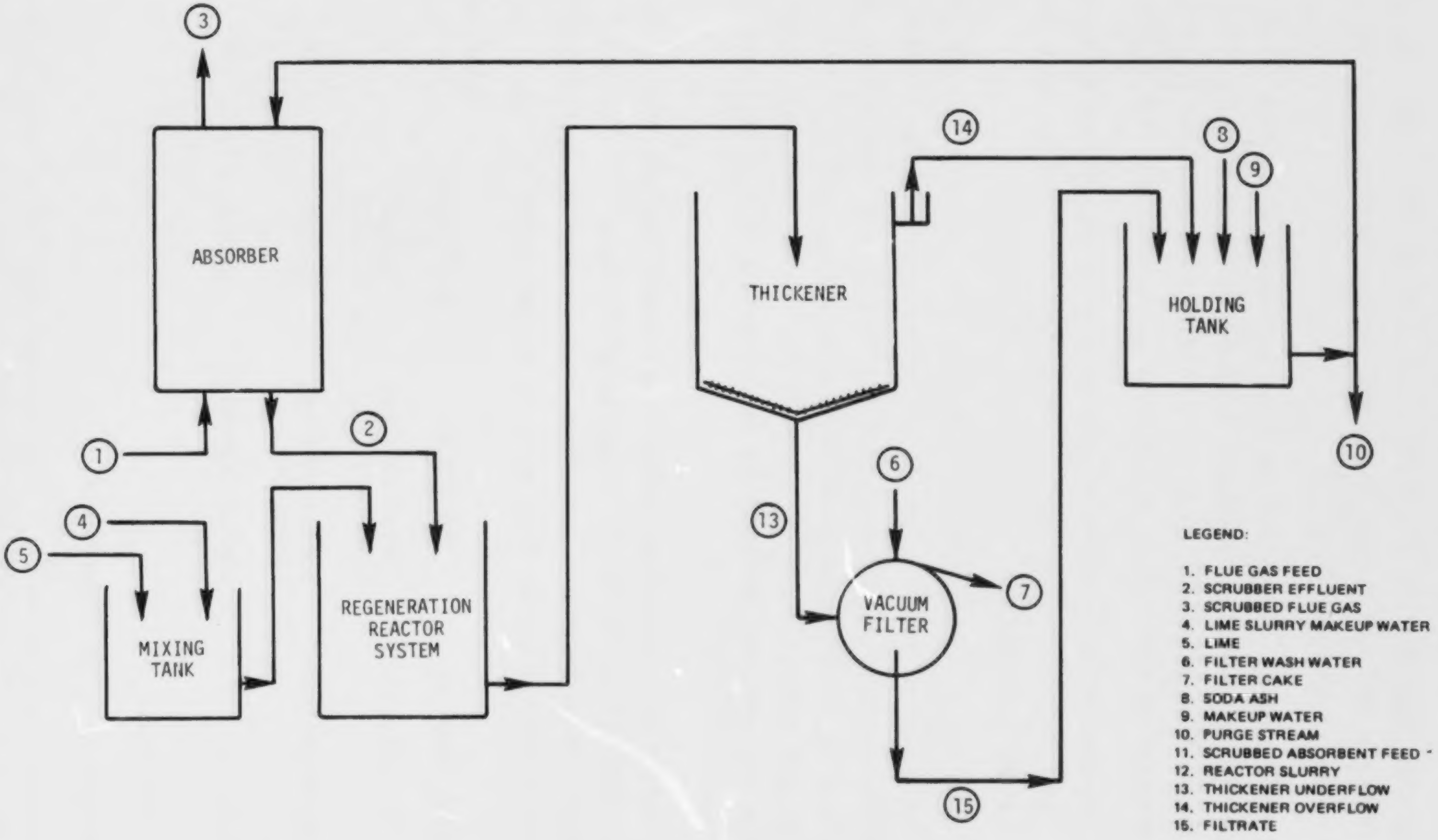
③
ABSORBER
①
②
④
⑤
MIXING TANK
REGENERATION REACTOR SYSTEM
THICKENER
⑬
⑭
⑥
VACUUM FILTER
⑦
⑮
⑧
⑨
HOLDING TANK
⑩
LEGEND:
1. FLUE GAS FEED
2. SCRUBBER EFFLUENT
3. SCRUBBED FLUE GAS
4. LIME SLURRY MAKEUP WATER
5. LIME
6. FILTER WASH WATER
7. FILTER CAKE
8. SODA ASH
9. MAKEUP WATER
10. PURGE STREAM
11. SCRUBBED ABSORBENT FEED
12. REACTOR SLURRY
13. THICKENER UNDERFLOW
14. THICKENER OVERFLOW
15. FILTRATE

Figure D-14. Dual Alkali Scrubbing with Lime Regeneration(11) absorbent stream (Stream 11). If fly ash removal is required, a venturi scrubber is installed upstream of the absorber. The fresh absorber feed solution consists of a mixture of sodium hydroxide, sodium sulfite, sodium sulfate, and a small amount of sodium carbonate.

SO_2 is absorbed by the active sodium constituents,* converting them to sodium bisulfite (Reactions 1, 2 and 3 below). Some oxidation of sodium sulfite to inactive sulfate also occurs in the scrubber (Reaction 4):

Absorber Reactions

(1) $Na_2CO_3 + 2SO_2 + H_2O \rightarrow 2NaHSO_3 + CO_2\uparrow$

(2) $NaOH + SO_2 \rightarrow NaHSO_3$

(3) $Na_2SO_3 + SO_2 + H_2O \rightarrow 2NaHSO_3$

(4) $Na_2SO_3 + 0.5\ O_2 \rightarrow Na_2SO_4$

A bleed stream from the scrubber hold tank (Stream 2) is pumped to a regeneration reactor where lime is added and calcium salts are precipitated by the following reactions:

Regeneration Reactions

(5) $Ca(OH)_2 + 2NaHSO_3 \rightarrow CaSO_3 \cdot 0.5H_2O\downarrow + Na_2SO_3 + 1.5\ H_2O$

(6) $Ca(OH)_2 + Na_2SO_3 + 0.5H_2O \rightarrow CaSO_3 \cdot 0.5H_2O\downarrow + 2NaOH$

(7) $Ca(OH)_2 + Na_2SO_4 + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O\downarrow + 2NaOH$

Sodium sulfate produced in the absorber is precipitated according to Reaction 7.

Slurry from the reactor (Stream 12) is pumped to a thickener where calcium salts are concentrated (Stream 13) and pumped to a rotary vacuum filter. A waste cake is produced (Stream 7), and some of the soluble sodium in the cake is washed back into the system (Stream 6). Filtrate (Stream 15) is combined with clear overflow solution from the thickener (Stream 14) and returned to the scrubber.

---

*Active sodium refers to sodium derived principally from NaOH, Na_2SO_3, $NaHSO_3$, Na_2CO_3 and $NaHCO_3$, as opposed to inactive forms derived from NaCl or Na_2SO_4. When active Na^+ is less than 0.15M, the system is considered to be in the dilute mode.

In some versions of the dual alkali process an additional liquid purge stream (Stream 10) is required to control sulfate and chloride buildup.

2.2 Equipment(4,8,12) - All equipment is conventional and includes venturi scrubbers - dual throat and variable throat types - sieve tray towers, FMC patented disc contactor towers, packed towers, agitated reactors, thickener with circulating rake, rotary vacuum filters, oil or steam type reheaters and demisters.

2.3 Field Stream Requirements

- Temperature(8,12): 408°K to 561°K (275°F-550°F)
- Pressure: atmospheric
- SO_2 Loading (dry basis)
  - Concentrated mode*(8,12): 1800-8000 ppm
  - Dilute mode(13): 250-400 ppm, up to 1500 ppm
- Particulate Loading
  - With venturi(4): 7.25 g/Nm^3 dry (3 gr/scf dry)
  - Without venturi†(8): 0.048 g/Nm^3 dry (0.02 gr/scf dry)
- Contaminant Limitations
  - Oxygen (dry basis)

    Concentrated mode(8,12): 6.5%-7.6% maximum

    Dilute mode: No upper limit; system favors high oxygen concentration.
  - Chloride ion(4,8): Harmful to equipment, not process. Successful prototype operation demonstrated with 0.5-0.10 weight % Cl coal, dry basis.

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*Concentrated mode dual alkali systems are not normally designed for flue gas streams with SO_2 concentrations less than about 1500 ppm or O_2 concentrations greater than about 7% because of the resulting high oxidation rates of sulfite to sulfate in the scrubber. Dilute mode systems are normally designed for low sulfur coals (SO_2 < 1500 ppm) because these systems regenerate sodium sulfate and make gypsum more efficiently.

†Assuming an electrostatic precipitator is used.

- Potassium ion(4): ?
- Fluoride ion(4): ?

2.4 Operating Parameters

- Absorption System
  - Temperature(7): Flue gas saturation temperature; for boiler flue gas, 328°K (130°F) is typical
  - Pressure: Atmospheric
  - Loading: Dilute mode(13) - L/G of 2.67 liters/m^3 (20 gal/1000 ACF)

    Concentrated mode(8,12) - L/G of 1.82 liters/m^3 (13.6 gal/1000 ACF), dual throat venturi; 0.67 - 1.34 liters/m^3 (5-10 gal/1000 ACF), tray tower
  - pH(8,12): 4.8 - 7.0
- Regneration System
  - Temperature: Same as absorber
  - Pressure: Atmsopheric
  - FMC Single Reactor (Concentrated Mode)

    pH(7): 8.5

    Residence time(12): 5 minutes
  - ADL/CEA Two Reactor System (Concentrated Mode)

    pH(8): 11.0 - 12.5

    Residence time(8): 5 minutes - Reactor 1
    35 minutes - Reactor 2

2.5 Process Efficiency and Reliability(8,14) - Concentrated mode dual alkali systems have demonstrated SO_2 removal capabilities over 99% for typical flue gas streams from coal-fired utilities. Lime utilization has ranged from 95%-100% based on one mole $Ca(OH)_2$/mole SO_2 removed.

A 3-MW prototype of the FMC process has had 94% availability for the initial year of operation, and a 50-MW commercial system started up in October 1975 and also had a high availability since that time. A 20-MW ADL/CEA prototype logged 78% availability over a 17 month test period.

2.6 Raw Material Requirement

- Makeup Chemicals(8,9,12,13)

  Na_2CO_3: 0.98-1.0 moles Ca/mole **sulfur** removed - concentrated mode; 1.0-1.1 Ca/S - dilute mode, generally. 1.4 to 1.65 Ca/mole sulfur dilite mode system actual operating data.

- Makeup Water: Depends heavily on type of system. System with separate particulate scrubber requires additional water. System for liquid purge for sulfate control (FMC) uses more water than system without sulfate purge.

- Air: Used only in dilute mode systems to oxidize all sodium sulfate to sulfate prior to regeneration by sparging.

2.7 Utility Requirements

- Steam: None typically, but can be used to reheat flue gas in lieu of fuel oil.

- Fuel Oil(4): 1.4% - 2.1% of energy input to a power generation station.

- Electricity(4,6,8): 1.3% - 2% of utility station generation for concentrated mode, tray tower system removing 95% of SO_2 produced from burning 3-4 wt % sulfur coal with no particulate removal. 2.5% - 3.0% of station generation for system removing both SO_2 and particulates.

3.0 Process Advantages(15)

- Capital and operating costs are relatively low. The process utilizes conventional chemical processing equipment and materials required are commonly used and available.

- Very high SO_2 removal efficiencies can be obtained. Tray towers can be designed for insertion or removal of extra trays to adjust to changing performance requirements.

- The soluble product in the absorber minimizes solids buildup and erosion problems.

- Process can simultaneously remove particulates and SO_2.
- A low L/G ratio is featured by the scrubber.
- Corrosion and erosion problems are minor compared to those in wet lime/limestone processes.
- High fly ash contents can be tolerated in the system.

4.0 Process Limitations(15)

- Large quantities of waste calcium sulfite and calcium sulfate salts containing soluble sodium must be disposed of.
- Design complexities must be introduced to deal with the following problems:
  1) Excessive purge of Na_2SO_4 produced as a result of oxidation (the ADL/CEA process does not require a purge stream when high sulfur coal is burned and less than 40% excess air is used in combustion of coal).
  2) Clean scrubbing liquor saturated with calcium sulfate. Excessively high levels of calcium sulfate could lead to scaling problems. (Concentrated mode systems do not scale as long as there is proper pH control.)
- Requires some makeup to replenish sodium losses.
- Problems of pitting and corrosion due to chloride buildup. Special coatings and linings and/or higher grade alloys must be used.
- Generates predominantly calcium sulfite solids - a material that does not occur naturally in nature, is thixotropic and has a high potential COD.

5.0 Process Economics

- General Motors Dilute Mode System(12): $3.5 million (1974) capital investment for "first-of-a-kind" industrial boiler system equivalent to 32 MW.

  Unit capital cost: $88/kw

  Operating costs: Not available
- FMC Concentrated Mode(12): Estimated cost for 150-MW utility boiler system is $6 million (1974). Unit capital cost: $40/kw
- EPA Estimates(9): Based on concentrated mode, dual alkali system, coal-fired power plant flue gas, 90% SO_2 removal, soda ash makeup, new 200 MW system, 80% load factor, throwaway $CaSO_3/CaSO_4$ salts

Unit capital cost: $50-60/kw (1974 dollars)

Operating cost: 2.5-3 mils/kwh

Actual costs are not available for full scale applications.

6.0 Input Streams

- Flue Gas (Stream 1): see Table D-23.
- Lime Slurry Makeup Water (Stream 4): Quantity depends on particular system water balance as determined by inlet flue gas temperature, sulfur dioxide concentration, waste cake moisture and wash requirements, sulfate and chloride purge requirements, demisters and pump seals.
- Lime (Stream 5): see Section 2.6.
- Filter Wash Water (Stream 6): Flow rate depends on system design requirements. Wash ratios of 3:1 or less are normal(7).
- Soda Ash Makeup (Stream 8): see Section 2.6.
- System Makeup Water (Stream 9): Rate depends on system with balance.

7.0 Intermediate Streams

- Scrubber Effluent (Stream 2): see Table D-24.
- Scrubber Regenerated Absorbent Feed (Stream 11): see Table D-25.
- Reactor Slurry (Stream 12): see Table D-26.
- Thickener Underflow Slurry (Stream 13):

	ADL/CEA-Gulf Power Prototype(8)
Solids Concentration	less than 30 wt %

- Thickener Overflow (Stream 14): see Table D-27.
- Filtrate (Stream 15): No data available.

8.0 Discharge Streams

- Flue Gas Outlet (Stream 3): see Table D-28.
- Filter Cake (Stream 7): see Table D-29.
- Liquid Purge (Stream 10): The only commercially available double alkali process in the U.S. requiring liquid purge is the FMC process in some applications. Characteristics are the same as for Intermediate Stream 11. See Table D-25. No specific data available.

TABLE D-23. CHARACTERISTICS OF FLUE GAS FEED TO DUAL ALKALI PROCESS

Parameter/ Concentration	General Motors - Parma, Ohio Demonstrator(12)	ADL/CEA Gulf Power Prototype(8)	FMC Pilot Plant(2)
Temperature	450°K (350°F) - two large boilers	408°K (275°F)	478°K (400°F)
	561°K (550°F) - two small boilers		
Flow Rate	101,880 m^3/hr (60,000 acfm) per large boiler	127,350 m^3/hr	4,377 m^3/hr
	84,900 m^3/hr (50,000 acfm) per small boiler	(75,000 acfm)	(2,578 acfm)
SO_2	900-1600 ppm, range	1800-3800 ppm, dry	3363 ppm
	1200-1300 ppm, average		
Particulate	0.725 g/Nm^3 (0.3 gr/scf)	0.048 g/Nm^3 dry (0.02 gr/scf dry) with precipitator energized	5.8 g/Nm^3 (2.4 gr/scf)
Composition			
O_2	--	6.5% max., dry	7.6%
N_2	--	--	76.3%
CO_2	--	--	11.4%
H_2	--	--	4.7%
SO_2	--	--	--

TABLE D-24. CHARACTERISTICS OF SCRUBBER EFFLUENT IN DUAL ALKALI PROCESS

Parameter/ Constituent	General Motors Parma, Ohio Demonstrator(12)	ADL/CEA Gulf Power Prototype(4,8)	FMC Pilot Plant(7,12)
Temperature	--	--	328°K (130°F)
pH	5.5 - 6.0	4.8 - 6.0	6 - 7
Chloride ion (Cl^-)	--	13,000 ppm, max.	--
Potassium ion (K+)	--	300 - 1300 ppm	--
Fluoride ion (F^-)	--	70 ppm, max.	--
Total sodium (Na^+)	--	--	>2M
Other non-Na, K, Ca metals	--	<1 ppm each	--
Active alkali	--	--	>0.5M
Sulfate ($SO_4^=$)	0.35M	--	--
Hydroxide (OH-)	Trace	--	--
Bisulfite (HSO_3^-)	0.03M	--	--
Calcium (Ca++)	300 - 400 ppm	--	--

TABLE D-25. CHARACTERISTICS OF REGENERATED ABSORBENT IN DUAL ALKALI PROCESS

Parameter/Constituent	General Motors - Parma, Ohio Demonstrator(12)
pH	9.0
Sulfate ($SO_4^=$)	--
Hydroxide (OH^-)	0.1M
Bisulfite (HSO_3^-)	Trace
Calcium (Ca++)	300 - 400 ppm

TABLE D-26. CHARACTERISTICS OF REACTOR SLURRY IN DUAL ALKALI PROCESS

Parameter/Constituent	ADL/CEA-Gulf Power Prototype(4,8)	FMC Pilot Plant(7,12)
No. Reactors in Series	2	1
Residence Time		
● Reactor 1	3-5 min.	5 min.
● Reactor 2	30-40 min.	Not applicable
pH	11.0 to 12.5	8.5
Solids Concentration	Up to 5%	--
Flow Rate	700 liters/min (185 gpm)	

TABLE D-27. CHARACTERISTICS OF THICKENER OVERFLOW IN DUAL ALKALI PROCESS

Parameter/Constituent	ADL/CEA-Gulf Power Prototype(8)
pH	11 - 12.5
Active Sodium (Na+)	0.2 - 0.6M
Sulfate ($SO_4^=$)	0.6 - 1.05M
Chloride ion (Cl^-)	4000 - 5000 ppm
Calcium ion (Ca^{++})	50 - 200 ppm

TABLE D-28. CHARACTERISTICS OF FLUE GAS IN DUAL ALKALI PROCESS

Parameter/ Constituent	General Motors Parma, Ohio Demonstrator(12)	ADL/CEA Gulf Power Prototype(8)	FMC Pilot Plant(12)
Temperature	Saturation temp.	Saturation temp.	Saturation temp.
Flow Rate	--		--
SO_2	20 - 200 ppm	-	343 ppm
Solids Entrainment	--	0.0085 g/Nm^3 (0.0035 gr/scf dry)	--
Liquid Entrainment	--	0.060 g/Nm^3 (0.025 gr/scf dry)	--
Sodium Entrainment	--	0.0048 g/Nm^3 (0.002 gr/scf dry)	--

TABLE D-29. CHARACTERISTICS OF FILTER CAKE IN DUAL ALKALI PROCESS

Parameter/ Constituent	General Motors-Parma, Ohio Demonstrator(12)	FMC Pilot Plant(12)	ADL/CEA Gulf Power Prototype(8)
$Ca(OH)_2$	10-20%, dry basis	--	--
Fly Ash	1-2%, dry basis	13.95%, wet basis	--
Solubles as Na_2SO_4	4-5%, dry basis	1.18%, wet basis	--
$CaSO_x$	Remainder of dry cake	--	--
Moisture	50%	35.80%, wet basis	--
Wash Efficiency	20% reduction of solubles	90% reduction (2 displacement washes)	up to 90% reduction (2-3) displacement washes)
$CaSO_3 \cdot 0.5\ H_2O$	--	47.93%, wet basis	--
$CaCO_3$	--	1.14%, wet basis	--
Insoluble Solids	~48%	~63%	50%, wet washed cake
Soluble Solids	--	--	3-5%, dry washed cake 12%, dry cake, unwashed
Total Solids	--	--	45 - 60%
$CaSO_4/CaSO_x$ (molar)	--	--	0.10 - 0.25

9.0 Data Gaps and Limitations

Complete data sets are not available for concentrated mode operation of double alkali processes, the most commercially viable mode. Only partial data are available from the 20 MW prototype system at Gulf Power, the largest successful, closed loop, dual alkali system operated on a coal-fired utility in the U.S. to date. In most cases, neither total gas analyses nor extensive trace component analyses have been conducted. Commercial data are not available for concentrated mode, closed loop operation. The concentrated process cannot operate closed loop on streams containing either a high oxygen content or a low sulfur dioxide concentration.

10.0 Related Programs

Arthur D. Little has an $800,000 contract from EPA to study waste salt fixation, disposal and utilization. Both ADL/CEA and FMC are constructing their first full-scale, commercial, utility-based processes.

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MAGNESIUM OXIDE PROCESS

1.0 General Information

1.1 Operating Principles(1) - Magnesium oxide slurry absorption of sulfur dioxide from flue gas, after particulate removal, in a wet scrubber. The aqueous slurry is centrifuged; spent magnesium solids are recovered and calcined at elevated temperature with coke to regenerate magnesium oxide crystals. An SO_2-rich gas stream is produced during regeneration.

1.2 Development Status - Currently available and commercially tested in the U.S. and Japan(1).

1.3 Licensor/Developer(1)

In the U.S.:	United Engineers and Contractors, Inc. Philadelphia, Pa. (Mag-Ox process)
	Chemico (Chemical Construction Co.) and Basic Chemicals
In Japan:	Onahama - Tsu Rishing Mitsui Mining Chemico-Mitsui

1.4 Commercial Applications(1,2,3)

- Chemico: Boston Edison Company operated a magnesium oxide scrubbing system at its Mystic Station in Everett, Mass. Chemico Air Pollution Control Company installed the system on Unit No. 6, a 150 MW oil-fired boiler unit. The unit was operated from April 1972 through June 1974. The regeneration facility for the Mag-Ox unit was located in Rumford, R.I.

  Potomac Electric Power Company operated a magnesium oxide scrubbing system at its Dickerson Station in Dickerson, Maryland on Unit No. 3, a 190 MW coal-fired boiler unit. Only 50 percent of the gas, or 95 MW equivalent, was processed through the scrubber. The system was operated from September 1973 to

August 1975. The regeneration facility utilized, the same as Boston Edison's, was located in Rumford, R.I.

- United Engineers: A demonstration program is in progress at Eddystone No. 1 boiler of Philadelphia Electric Company. Pending the outcome of the scheduled one-year test program, full-scale application of the process may result at this station and at Cromby. The present system is 120 MW in capacity. United Engineers has a total of four Mag-Ox plants in operation in the United States on 846 MW total capacity.

  In Japan, both Onahama-Tsu Rishing and Mitsui Mining have one plant each using the magnesium oxide process and producing sulfuric acid as the byproduct. Chemico-Mitsui has one plant using magnesium oxide as absorbent and producing sulfur.

2.0 Process Information

2.1 Flow Diagram - see Figures D-15, D-16 and D-17.

- Process Description(2,3) - In the United Engineers version of the Mag-Ox Process, hot flue gas enters the particulate scrubber where it is contacted with water, removing the majority of particulate matter. Most of the hydrogen chloride, a variable fraction of the sulfur trioxide and a minor amount of the sulfur dioxide contained in the flue gas are absorbed in the particulate scrubbing liquor. Caustic soda is added to control solution pH and prevent corrosion. A liquid blowdown stream is taken off the particulate scrubber at a rate sufficient to prevent excessive chloride buildup. This stream is neutralized and sent to the station ash settling basin.

  The flue gas from the particulate scrubber is contacted with an aqueous slurry of magnesium sulfite to remove better than 90% of the sulfur dioxide in the flue gas:

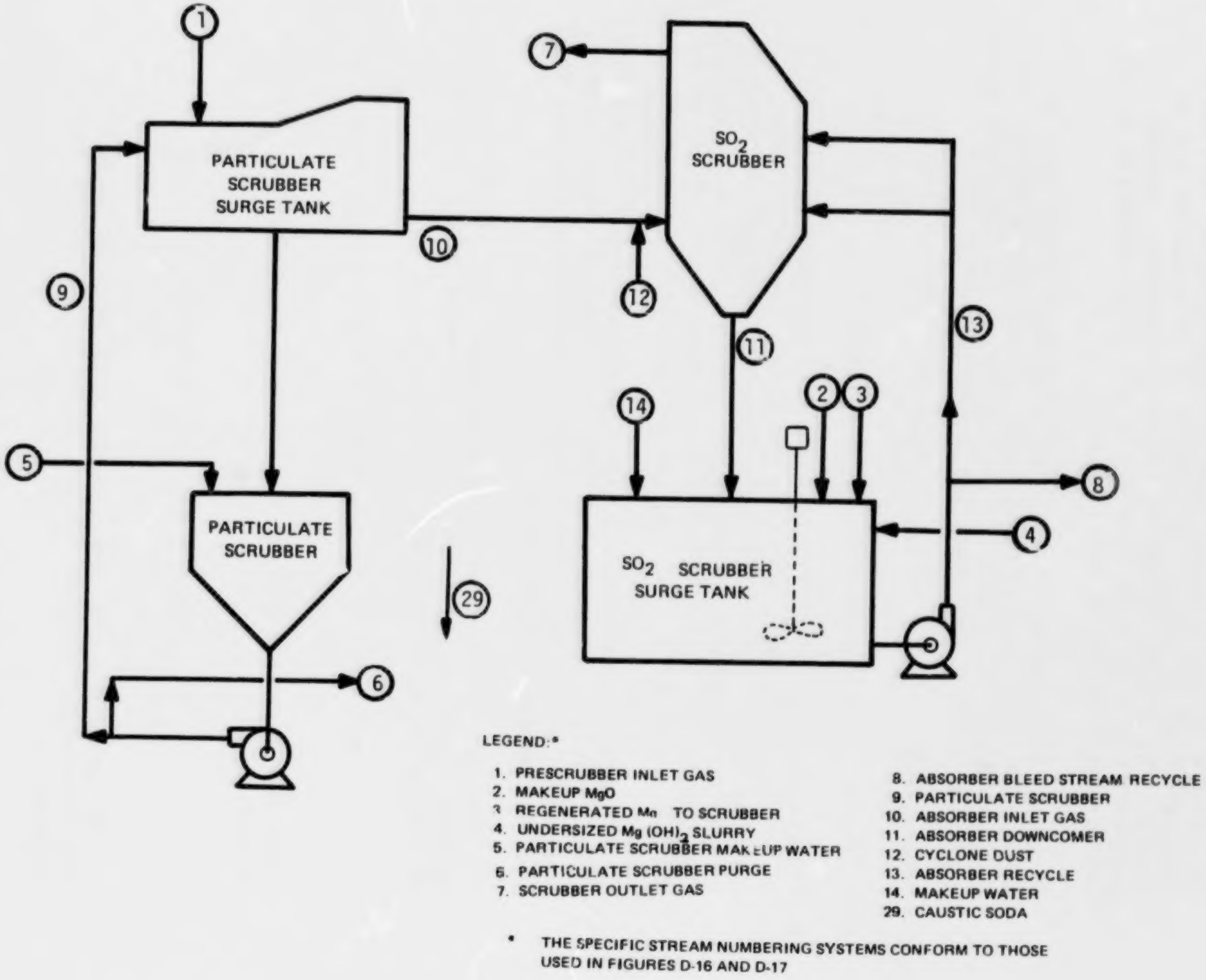
$$MgO + SO_2 + H_2O = MgSO_3 \cdot \eta H_2O, \quad \eta = 3 \text{ or } 6$$

  Insoluble magnesium sulfite is converted to soluble magnesium bisulfite:

$$MgSO_3 + SO_2 + H_2O \rightarrow Mg(HSO_3)_2$$

  In the scrubber surge tank slaked magnesium oxide is added to the circulating scrubber liquor, converting bisulfite back to sulfite:

$$Mg(HSO_3)_2 + MgO \rightarrow 2\, MgSO_3 + H_2O$$

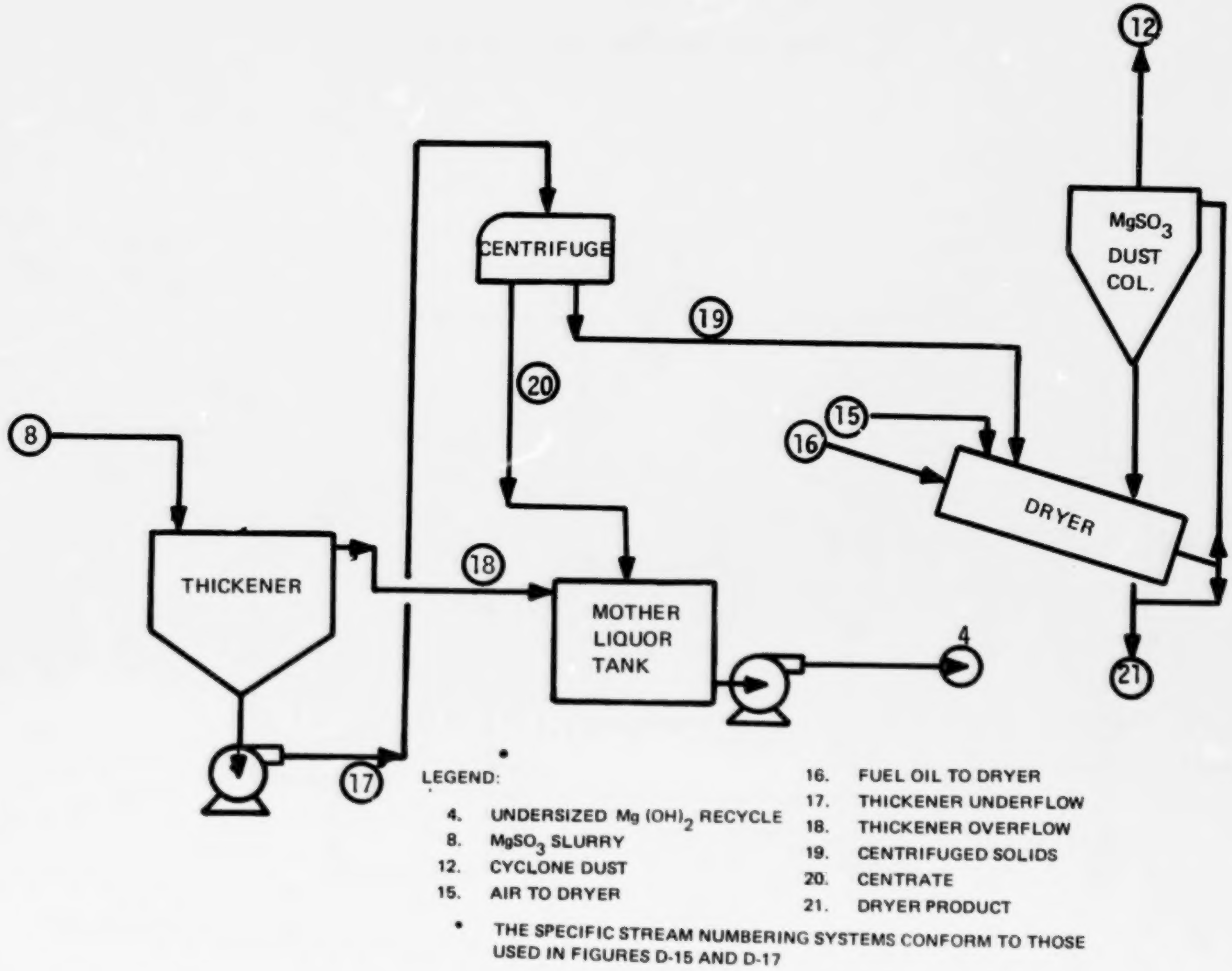

①
PARTICULATE SCRUBBER SURGE TANK
⑨
⑩
⑤
PARTICULATE SCRUBBER
⑥
㉙
⑦
SO2 SCRUBBER
⑫
⑪
⑬
⑭
② ③
SO2 SCRUBBER SURGE TANK
⑧
④

LEGEND:*

1. PRESCRUBBER INLET GAS
2. MAKEUP MgO
3. REGENERATED Mg TO SCRUBBER
4. UNDERSIZED $Mg(OH)_2$ SLURRY
5. PARTICULATE SCRUBBER MAKEUP WATER
6. PARTICULATE SCRUBBER PURGE
7. SCRUBBER OUTLET GAS
8. ABSORBER BLEED STREAM RECYCLE
9. PARTICULATE SCRUBBER
10. ABSORBER INLET GAS
11. ABSORBER DOWNCOMER
12. CYCLONE DUST
13. ABSORBER RECYCLE
14. MAKEUP WATER
29. CAUSTIC SODA

* THE SPECIFIC STREAM NUMBERING SYSTEMS CONFORM TO THOSE USED IN FIGURES D-16 AND D-17

Figure D-15. Magnesium Oxide Scrubber System(3)


12
MgSO$_3$
DUST
COL.
CENTRIFUGE
19
20
8
15
16
DRYER
THICKENER
18
MOTHER
LIQUOR
TANK
4
21
17

LEGEND:

4. UNDERSIZED Mg (OH)$_2$ RECYCLE
8. MgSO$_3$ SLURRY
12. CYCLONE DUST
15. AIR TO DRYER
16. FUEL OIL TO DRYER
17. THICKENER UNDERFLOW
18. THICKENER OVERFLOW
19. CENTRIFUGED SOLIDS
20. CENTRATE
21. DRYER PRODUCT

- THE SPECIFIC STREAM NUMBERING SYSTEMS CONFORM TO THOSE USED IN FIGURES D-15 AND D-17

Figure D-16. Magnesium Oxide Process - MgSO$_3$ Recovery System$^{(3)}$

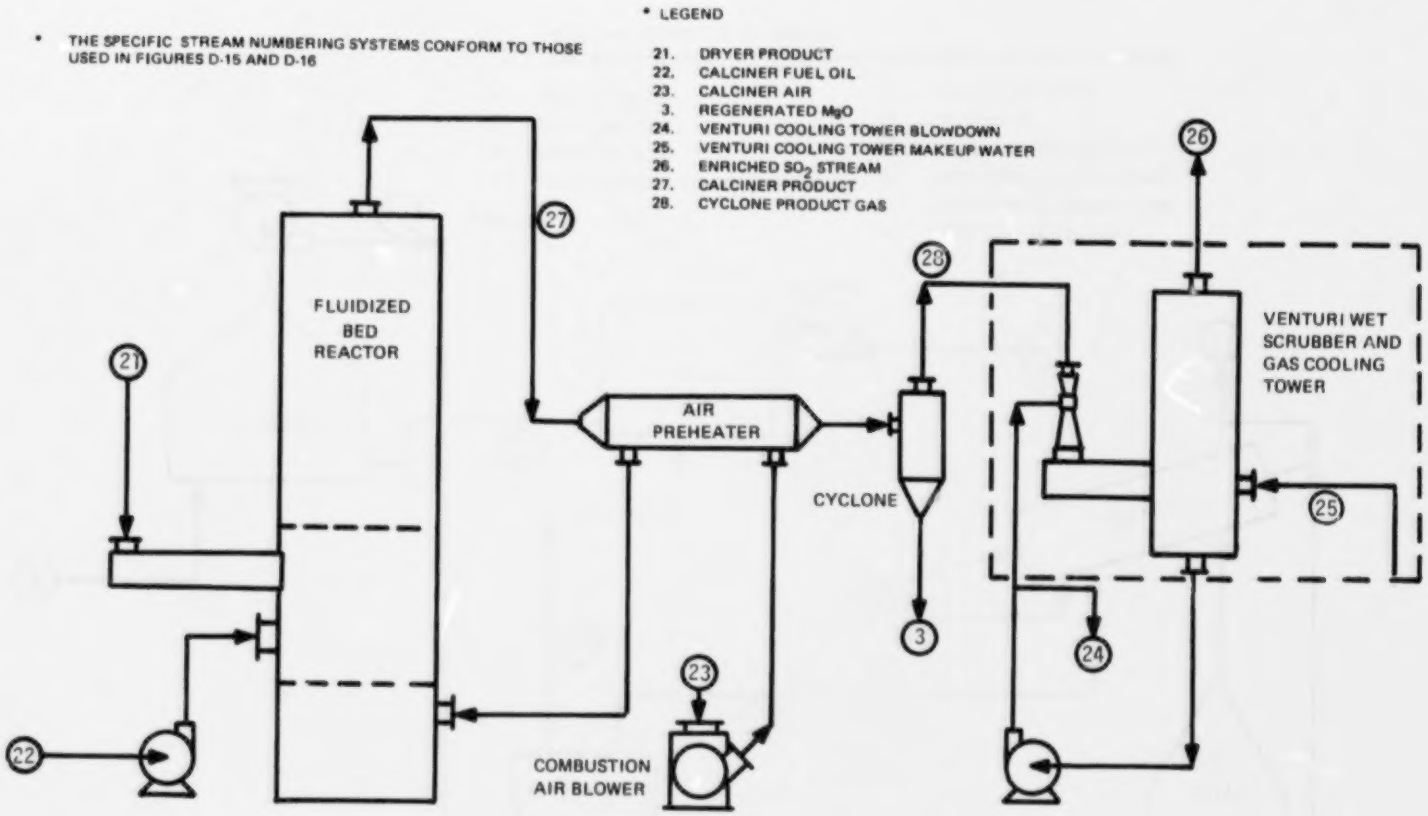

• THE SPECIFIC STREAM NUMBERING SYSTEMS CONFORM TO THOSE USED IN FIGURES D-15 AND D-16
• LEGEND
21. DRYER PRODUCT
22. CALCINER FUEL OIL
23. CALCINER AIR
3. REGENERATED MgO
24. VENTURI COOLING TOWER BLOWDOWN
25. VENTURI COOLING TOWER MAKEUP WATER
26. ENRICHED SO2 STREAM
27. CALCINER PRODUCT
28. CYCLONE PRODUCT GAS
FLUIDIZED BED REACTOR
AIR PREHEATER
CYCLONE
COMBUSTION AIR BLOWER
VENTURI WET SCRUBBER AND GAS COOLING TOWER
21
22
23
27
28
3
24
25
26

Figure D-17. MgO Regeneration Plant(3)

A bleed stream from the scrubber slurry proceeds to a thickener, centrifuge and rotary kiln where magnesium sulfite is removed as a dry product. Some of the sulfite is oxidized to sulfate:

$$MgSO_3 + 1/2\ O_2 \rightarrow MgSO_4$$

The dry crystals are calcined in a fluid bed reactor by the following reaction:

$$MgSO_3 \xrightarrow{\Delta} MgO + SO_2 \uparrow$$

The regenerated magnesium oxide crystals are separated from the SO_2-rich gas stream. The gas stream is scrubbed and cooled prior to transfer to a suitable conversion facility.

The Mag-Ox process developed by Chemico differs somewhat from the United Engineers process. A side stream of the magnesium sulfite (hydrate) is separated and sent to a centrifuge. Also, carbon (coke) is added to the feed stream to the calciner to improve sulfate regeneration:

$$MgSO_4 + 0.5\ C \xrightarrow{\Delta} MgO + 0.5\ CO_2 + SO_2 \uparrow$$

2.2 Equipment - Most of the equipment in the Mag-Ox process is conventional, such as the variable throat venturi, scrubber, thickener, surge tanks, centrifuges, cyclones, cooling towers/wet scrubber and the dryer. Some of the equipment must be altered to handle magnesium slurries and its associated problems. One item of equipment, the fluidized bed reactor, is specifically designed for this use.

2.3 Feed Stream/Requirements

- Temperature(3,4) - 400°K-440°K (250°F-330°F) typically, from utility boiler
- Pressure - near atmospheric
- Loading(5) - 0.06 to 4.5 gr/SCF (0.145 to 10.9 g/Nm^3) dry particulate acceptable to first stage particulate scrubber. Systems have been designed for 1850 ppm SO_2 range but can be designed for much higher loadings.
- Contaminant Limitation - ?

2.4 Operating Parameters

- Particulate Scrubbing Step
  - Temperature(3): 326°K-328°K (125°F-130°F)
  - Pressure drop(3):* liquid 254-305 mm H_2O (10-12 in. H_2O)
  - pH(3): 2.8 to 3.1
  - Slurry concentration(3): 2%
  - L/G(3):† 0.65 liters/m^3 (4.85 gal/1000 ACF outlet)
  - Turndown: ?
- Absorption Step
  - Temperature (slurry)(5): 320°K (120°F)
  - Pressure drop(3):‡ 254 mm H_2O (10 in. water total), 5 in. per stage)
  - pH(3): about 6.3
  - Slurry concentration(3): 5-10 wt % magnesium sulfite
  - L/G(3): 6.5 liters/m^3 (48.5 gal/1000 ACF out)
  - Turndown: ?
- Drying Step
  - Temperature(5): 500°K (450°F) off-gas
  - Mass throughput rate: ?
- Regeneration Step
  - Temperature(3): 1230°K (1750°F)
  - Mass throughput rate: ?

---

*Pressure drop is for variable thraot venturi scrubber or Environeering Ventri-Rod unit. Both types are in service .

†L/G is liquid-to-gas ratio.

‡Pressure drop is for two-stage Environeering Ventri-Rod unit.

2.5 Process Efficiency and Reliability(3,6) - Based on the magnesium oxide scrubbing system installed at the Eddystone Station of Philadelphia Electric Co. in mid-1971, the cumulative availability of 32% has been disappointing. Many operating difficulties have been encountered despite high particulate removals (97%-98%) and sulfur dioxide removal (greater than 95%). The longest continuous run has been 140 hours. Particulate removal efficiency is based on an outlet stream from the 93% efficient mechanical/electrostatic precipitator system. Also, most of the hydrogen chloride and some of the sulfur trioxide are removed in the particulate scrubber.

A Chemico-Mitsui plant at Idemitsu in Japan reports operability of 100% for a system operating an oil burner and Claus furnace gases.

2.6 Raw Material Requirements

- MgO Makeup(5) - 7% replacement per year.
- Coke - ?
- Caustic Soda - ?
- Lime - ?

2.7 Utility Requirements

- Electricity(5,6) - About 2% to 3% of station generating capacity. Pump and fan power usage at a Japanese plant treating Claus furnace and oil burner gases is 11.7 kwh/Nm^3 (0.31 kwh/scf).
- Process Water
  - Particulate scrubber: ?
  - Absorber: ?
- Air
  - Dryer: ?
  - Calciner: ?
- Fuel Oil
  - Dryer: ?
  - Calciner: ?

- Total: 9.8 liters/mwh (2.6 gal/MWH) of No. 2 fuel oil. However, No. 6 oil can be substituted(5). 311°K (100°F) reheat required at Philadelphia Electric's Eddystone plant(3).

2.8 Miscellaneous

- Oxidation(3) - Sulfite oxidation has been reported at around 15% (during drying).

3.0 Process Advantages(5)

- Minor disposal problems since MgO is regenerated and sulfur is recovered in a usable form.
- Sulfur can be recovered as high grade sulfuric acid or as elemental sulfur.
- Regeneration can be carried out at a remote site, thus permitting use of a central regeneration facility serving several FGD units.
- Only minor plugging and scaling problems encountered in the scrubber.

4.0 Process Limitations(5)

- Energy requirements are relatively high.
- Past demonstrations at Boston Edison and Potomac Electric's Dickerson Station exhibited relatively low reliability.
- Difficulties with the centrifuged $MgSO_3 \cdot \eta H_2O$ cake (η=3 or 6) because the trihydrate and hexahydrate crystals have different handling properties.
- Corrosion problems in the slurry-handling systems.
- Regenerated and makeup MgO is required in a pulverized form.
- The scrubber requires a high liquid-to-gas ratio.
- Fly ash must be kept out of the regeneration system, thus necessitating extensive particulate removal prior to gas processing.

5.0 Process Economics

A 1973 EPA study provided the following costs(7):

Capital investment:	\$33-66/kw
Operating costs:	1.6-3.0 mils/kwh - no credit for sulfur recovery 1.4-2.8 mils/kwh - with credit for sulfur recovery

In another more recent study, estimated costs of providing 1420 MW's (gross) of scrubber service, excluding acid plant, for the Potomac Electric Power Company's Dickerson Station is $106/kw (1975 dollars). Operating cost was estimated at 5.0 mils/kwh(5).

Total capital cost for Philadelphia Electric's Eddystone plant is estimated to be about $130/kw, including particulate scrubbing and a sulfuric acid facility. Also included is about a $20/kw retrofit charge. The operating and maintenance cost of the Eddystone scrubber is estimated at about 2.3 mils/kwh excluding any credit for by-product sulfuric acid. If credit is taken for by-product acid, then the O&M cost drops to 2.0 mils/kwh. Use of a more normal 283°K (50°F) reheat instead of the 311°K (100°F) used at Eddystone would reduce the cost an additional 10%(3).

6.0 Input Streams (see Figures D-15, D-16 and D-17)

- Prescrubber inlet gas (Stream 1) - see Section 2.3.

	Potomac Electric-Dickerson(4)	Philadelphia Electric-Eddystone(3)
Temperature:	400°K (250°F)	420°K-440°K (300°F-330°F)
Flow Rate:	500,000 m^3/hr (295,000 acfm)	545,000 m^3/hr (321,000 acfm)
SO_2:	1700 ppm, 3% sulfur coal	Derived from 2.6% sulfur coal, dry
Particulate:	0.145 g/Nm^3 (0.06 gr/scf dry) with precipitator operating 10.8 g/Nm^3 (4.5 gr/scf dry) without precipitator	90.7 kg/hr (200 lb/hr)

- Makeup MgO (Stream 2) - ?
- Particulate Scrubber Makeup Water (Stream 5) - ?
- Absorber Makeup Water (Stream 14) - ?
- Dryer Air (Stream 15) - ?
- Dryer Fuel Oil (Stream 16) - ?
- Calciner Fuel Oil (Stream 22) - ?
- Calciner Air (Stream 23) - ?

- Venturi Cooling Tower Makeup Water (Stream 25) - ?
- Caustic Soda (Stream 29) - ?

7.0 Intermediate Streams (see Figures D-15, D-16 and D-17)

- Absorber Bleed Stream (Stream 8)

	Philadelphia Electric-Eddystone(3)
pH:	~6.3
$MgSO_3$ concentration	5 - 10 wt %
Sulfate concentration:	2,000 - 5,000 ppm

- Particulate Scrubber Recycle (Stream 9) - see Discharge Stream 6
- Absorber Inlet Gas (Stream 10)

	Potomac Electric-Dickerson(4)	Philadelphia Electric-Eddystone(3)
Temperature:	320°K (120°F)	330°K (130°F)
Flow Rate:	--	455,000 m^3/hr (268,000 acfm)
Particulate:	--	14 kg/hr (30 lb/hr)

- Absorber Downcomer (Stream 11) - ?
- Absorber Recycle (Stream 13) - ?

	Philadelphia Electric-Eddystone(3)
pH:	5.8 - 6.8
Flow Rate:	50,658 liters/min (14,000 gpm)

- Cyclone Dust (dryer) (Stream 12)

	Potomac Electric - Dickerson(4)
Temperature:	500°K (450°F)

- Undersized $Mg(OH)_2$ Slurry (Stream 4) - ?
- Thickener Underflow (Stream 18) - ?

- Centrifuged Solids (Stream 19) - ?
- Centrate (Stream 20) - ?
- Dryer Product (Stream 21) - ?
- Regenerated MgO (Stream 3) - ?
- Calciner Product (Stream 27) - ?
- Cyclone Product Gas (Calciner) (Stream 28) - ?

8.0 Discharge Streams (see Figures D-15, D-16, and D-17)

- Particulate Scrubber Purge (Stream 6)

	Philadelphia Electric - Eddystone(3)
Temperature:	325°K-328°K (125°F-130°F)
pH:	2.8 - 3.1
Slurry concentration:	2 wt %
Chloride concentration:	< 1000 ppm

- Scrubber Outlet Gas (Stream 7)

	Philadelphia Electric - Eddystone(3)
Temperature:	325°K-328°K (125°F-130°F)
Flow Rate:	469,000 m^3/hr (276,000 ACFM)
Particulate:	< 0.18 g/1000 kcal (< 0.1 lb/MM Btu); 13.6 kg/hr (30 lb/hr)

- Venturi Cooling Tower Blowdown (Stream 24) - ?
- Enriched SO_2 (Stream 26) - ?

9.0 Data Gaps and Limitations

Incomplete composition data are currently available for most streams in the Magnesium Oxide (Mag-Ox) Scrubbing Processes. Data pertaining to feed stream pressure, contaminant limitations, scrubber turndown ratio, are missing. Dryer gas velocity, mass throughput rate, turndown ratio and fuel requirement are missing. Calciner pressure drop, superficial gas velocity, and fluidized bed height data are missing. Other missing data include material requirements for coke, caustic soda and lime, (when required), and process water usage. At present, there are no full scale commercial Mag-Ox Scrubber systems in operation in the U.S. To date, units have only been tested on utility flue gases. However, the process is regenerative and thus is closely tied into an elemental sulfur or sulfuric acid plant. At a coal gasification facility it would be possible to use a central sulfur plant for the Mag-Ox plant and for acid-gas treatment enriched gas. Particulate scrubber, absorber and system makeup and air flow rates required for dryer and calciner operations are unknown.

10.0 Related Programs

None known in the U.S. Commercial scale processes are in operation in Japan.

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Particulate Control Module

Fabric Filtration
Electrostatic Precipitation
Venturi Scrubbing
Cyclones

FABRIC FILTRATION PROCESS

1.0 General Information

1.1 Operating Principles - Physical removal of particulates from a gas stream by impaction, interception, diffusion and/or electrostatic attraction(1).

1.2 Developmental Status - Commercially available.

1.3 Licensor/Developer - Many companies manufacture fabric filtration systems, each system incorporating certain proprietary features. A complete listing of manufacturers are presented in technical and trade journals (e.g., Ref. 2).

1.4 Commercial Applications - Fabric filtration has been applied to coal fired boilers, coal loading and transport facilities, coal processing(3), and a large number of miscellaneous industrial gas cleaning operations.

2.0 Process Information

2.1 Flow Diagram - See Figure D-18.

- Process Description - Fabric filters are a series of tubular or envelope shaped bags contained in a structure called a baghouse. The filters or bags can be constructed of a variety of fibers, depending on design requirements. Table D-30 presents a limited selection of fabrics with their relative costs and properties for various applications(4) A variety of methods (both continuous and intermittent) are used for bag cleaning.*

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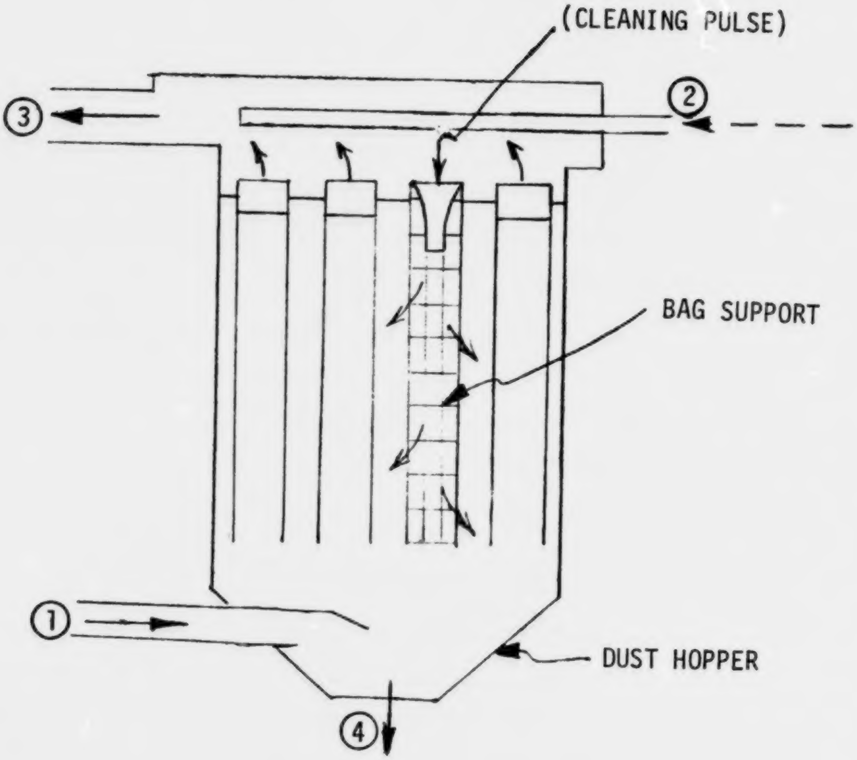
*Bag cleaning methods include use of shakers, high velocity reverse air flow, sonic energy and ring type spargers. These can be employed on both continuous and intermittent bases.


(CLEANING PULSE)
③
②
BAG SUPPORT
①
DUST HOPPER
④

LEGEND:

1. Dirty Gas
2. High Pressure Air (for bag cleaning)
3. Cleaned Gas
4. Collected Dust

Figure D-18. Continuous Cleaning Bag Filter

TABLE D-30. FILTER FABRIC PROPERTIES(5)

Fabric	Operating Temperature* (°F)	Acid Resistance	Alkali Resistance	Flex and Abrasion
Cotton	180	Poor	Very Good	Very Good
Wool	200	Very good	Poor	Fair to Good
Nylon	200	Fair	Excellent	Excellent
Dacron	275	Good in most acids, conc. H_2SO_4 partially dissolves fabric	Good in weak alkali, fair in strong	Very good
Orlon	260	Good to excellent	Fair to good	Good
Creslan	250	Good	Good	Good to very good
Dynel	160	Excellent	Excellent	Fair to good
Polypropylene	200	Excellent	Excellent	Excellent
Teflon	450	Excellent	Excellent	Fair
Fiberglas	500	Fair to good	Fair to good	Fair
Filtron	270	Good to excellent	Good	Good to very good
Nomex	375	Fair	Excellent at low temperature	Excellent

*Continuous operating temperature as recommended by the IGC.

2.2 Equipment - Bags, structure and bag cleaning device. All equipment is usually supplied by the manufacturer.

2.3 Feed Stream Requirements*

Temperature:	to 700°K (800°F)
Pressure:	None
Gas composition:	Wet, corrosive, explosive or oily gases are not well suited for treatment in a baghouse. However, design and operation modifications can be employed which will make treatment of most gases possible, although in some cases very expensive.

2.4 Operating Parameters - As above except:

Pressure: Pressure drop through the filter ranges from about 0.5 KPa (2 in. H_2O) to 2.4 KPa (10 in. H_2O).

2.5 Process Efficiency and Reliability†

- Efficiency(6)

Particle Mean Diameter	Control Efficiency
0.25	98.5% - 99.7+%
0.50	98.7% - 99.5+%
0.75	99.1% - 99.5+%
1.00	99.0% - 99.5+%
Above 100	99.5+%

- Reliability - Many years of use have proven that well designed, operated and maintained fabric filters can provide trouble-free service in many varied industrial applications.

2.6 Raw Material Requirements - None.

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*Requirements are dependent on fabric used; the figures given represent the maximums which could be handled by commercially available bags.

†Reliability and efficiency will be dependent on the specific fabric filtration design and on gas stream characteristics such as: chemical composition, site distribution, water vapor content, temperature, etc. Values given report results of a range of applications.

2.7 Utility Requirements(1)

- Electricity: Dependent on gas flow rate, pressure, and cleaning method.
- High pressure (for bag cleaning): Dependent on above factors. Not used in all designs.

2.8 Miscellaneous - Maintenance needs are dependent on the fabric selected and the nature of the gas being handled.

3.0 Process Advantages

- High efficiency on fine particulates.
- Low energy requirements.
- Can be adapted to a wide range of gas stream characteristics.
- Proven system; considerable experience has been acquired in a wide range of applications.

4.0 Process Limitations

- Requires large structures for high volume flows.
- Bag replacement required.
- Cannot handle explosive, corrosive or wet gas mixtures without special design considerations (e.g., control of temperature, use of proper fabrics, and selection of proper cleaning methods).
- Not suitable for operation at relatively high temperatures (generally above 550); temperatures limited, dependent on fabric selected.

5.0 Process Economics* - Installed costs for fabric filters have been reported to vary from \$50.76 to \$80.26 per actual cubic meter per minute (\$1.48 to \$2.34 per acfm)(6). The combined operating and maintenance costs are reported as \$12.36 to \$17.65 per actual cubic meter per minute (\$0.35 to \$0.50 per acfm) on an annualized basis(4)

6.0 Input Streams - Basis for stream compositions (input and discharge) is the same unit as in Section 5.0 (Process Economics), operating on a coal fired industrial boiler.

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*The costs presented are in early 1974 dollars and for a 39,100 Nm^3/hr (70,000 acfm) unit operating at 395°K (250°F) using Nomex^R felt bags.

6.1 Feed Gas Stream No. 1(7) - see Table D-31.

6.2 High Pressure Air Stream No. 2(7) - High pressure air; varies with manufacturer.

TABLE D-31. INPUT AND DISCHARGE STREAM CHARACTERISTICS FOR BAGHOUSE FILTRATION(7)

Particle Mean Diameter, μm	Inlet Loading mg/scf	Outlet Loading mg/scf	Removal Efficiency, %
79.5	4.221	0.0068	99.84
6	2.292	0.0060	99.74
4	1.482	0.003	99.78
2.8	1.254	0.0039	99.69
<0.9	3.2557	0.0221	99.31
		Overall Efficiency =	99.55

7.0 Discharge Streams

7.1 Cleaned Gas Stream No. 3(7) - see Table D-31.

7.2 Collected Dust Stream No. 4 - Dry collected dust quantity (rate) dependent on particle loading and removal efficiency.

8.0 Data Gaps/Limitations

Extensive performance data are available for fabric filtration applications to a variety of industrial gas cleaning operations. Evaluation of expected performance of the system in applications to coal gasification plant gas streams (e.g., coal and ash lockhopper vent gases) requires data on detailed characteristics of the gases to be treated. Such data which include gas temperature, particle size distribution and chemical characteristics of the gas stream including the particulates, are generally either not available or are incomplete.

9.0 Related Programs

Acurex/Aerotherm Corporation and Westinghouse are both presently involved in research programs to develop high temperature and pressure fabric filtration devices(8).

REFERENCES

1. Simon, H., Baghouses, Air Pollution Engineering Manual; AP-40, p. 106.

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3. Lear Siegler Inc., Installations of LUHR System Bag Houses , LUHR/PL/002A/9/74, September 1974.

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5. Reigel, S.A. and R.P. Bundy, Why the Swing to Baghouses, Power, January 1977, pp. 68-73.

6. Turner, J.H., Extending Fabric Filter Capabilities, JAPCA, 24:1182, 1974.

7. McKenna, J.D., et al, Performance and Cost Comparisons Between Fabric Filters and Alternate Particulate Control Techniques, JPACA, 24:1144, 1974.

8. Bush, J.R., Future Need and Impact on the Particulate Control Equipment Industry Due to Synthetic Fuels, paper presented at the 3rd Symposium on Environmental Aspects of Fuel Conversion Technology, Hollywood, Florida, September 1977.

ELECTROSTATIC PRECIPITATION PROCESS

1.0 General Information

1.1 Operating Principle - The removal of particulates from a gas stream by imposing an electrical charge and collecting the charged particles on oppositely charged collector plates.

1.2 Development Status - Commercially available.

1.3 Licensor/Developer - Many companies are involved in the commercial production of electrostatic collection devices. Complete listing can be obtained in various trade and technical journals (e.g., Ref. 1).

1.4 Commercial Applications - Electrostatic precipitators have been used to control particulate emissions in a wide range of industrial applications including: electrical power generation, cement making, steel making, smelting and the pulp and paper industries(2).

2.0 Process Information

2.1 Flow Diagram - see Figure D-19.

2.2 Equipment - Support structure, electrodes, collection bin, power supply (rectifier) and controls.

2.3 Feed Stream Requirements

- Temperature: precipitators have been applied at temperatures from ambient to about 700°K (800°F)(2,3).
- Pressure: precipitators have been applied on only a limited basis above atmospheric pressure. It has been reported that pilot and full scale tests have been successful at up to 55 atm(4).

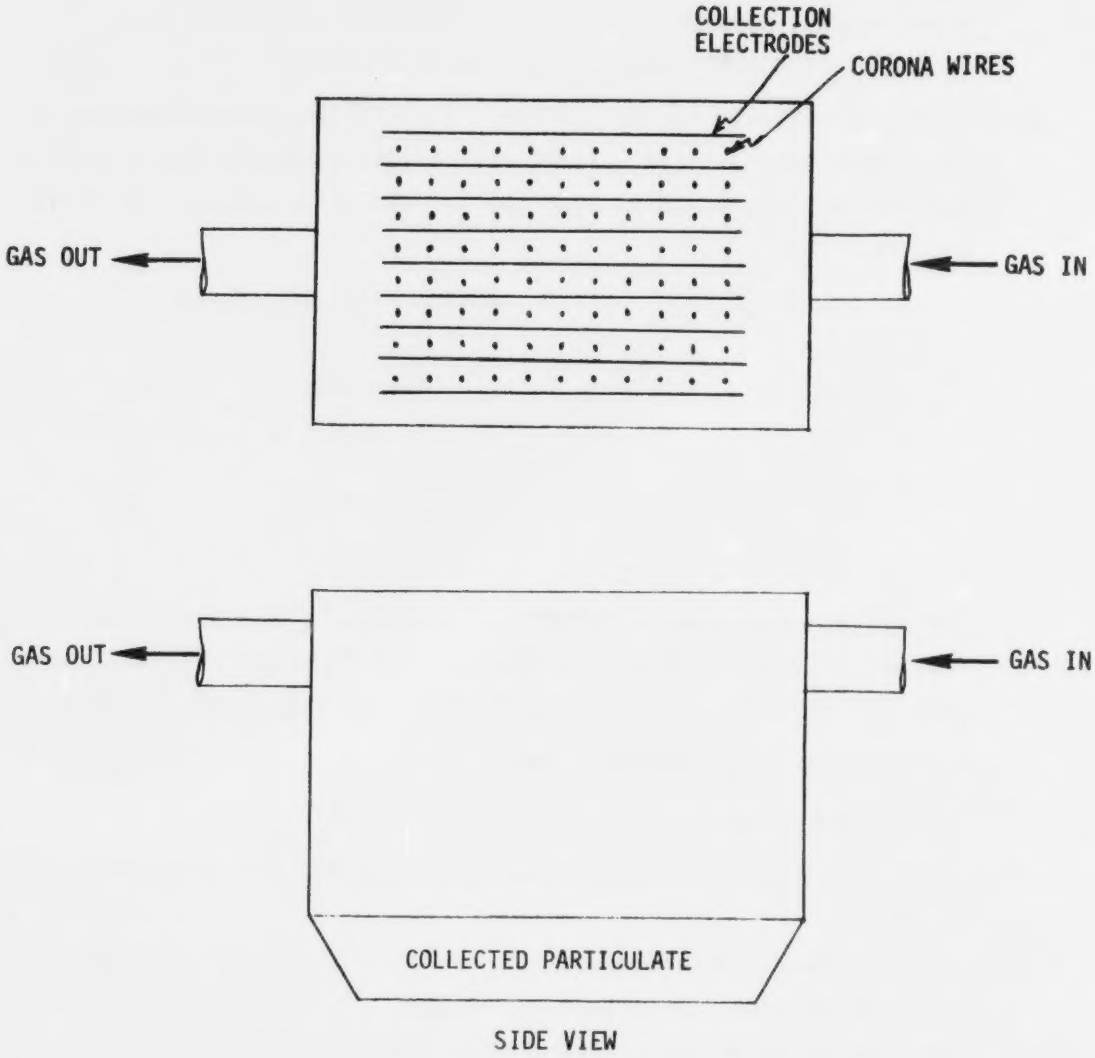
COLLECTION ELECTRODES
CORONA WIRES
GAS OUT
GAS IN
GAS OUT
GAS IN
COLLECTED PARTICULATE
SIDE VIEW

Figure D-19. Typical Electrostatic Precipitator

- Nature of particulate matter: The electrical resistivity* of particles should be between 10^9 and 10^{10} ohm-cm for optimum operation. The addition of certain additives (such as SO_3) can act to correct resistivity problems.

2.4 Operating Parameters - Precipitators have been operated in the above ranges; considerable testing will need to be done for operation at higher temperatures and/or pressures.

2.5 Process Efficiency and Reliability(5) - Efficiency is dependent on gas stream and particle parameters. Values given are for a range of applications operating on both the hot and cold side of coal fired boilers.

Particle Mean Diameter, μm	Collection Efficiency Range %
0.1	90 - 99.4
0.5	90 - 98.7
1.0	95 - 99.6
above 5.0	98 - 99.9

The system is generally reliable if operated near design conditions. Changes in particle size distribution, particle resistivity, flow rate and/or temperature can cause severe changes in performance.

2.6 Raw Material Requirements - None.

2.7 Utility Requirements

- Electricity: for corona power plus the pressure drop through unit.

2.8 Miscellaneous - Maintenance needs are relatively high as compared to other particulate collection devices. This is due mainly to the complexity of the system and the precipitators inability to accept changes in process parameters(6).

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*Electrical resistivity is a function of temperature as well as particle composition, therefore tests are usually performed on the actual gas stream before detailed design of the precipitator is performed.

3.0 Process Advantages(6)

- Highly effective collection
- High efficiency on small particles
- Low energy consumption (pressure drop is less than 25% of a fabric filter)
- Easy expandability

4.0 Process Disadvantages(6)

- High capital expenditures and space requirements
- Sensitivity to process upsets or changes
- Relatively high maintenance costs

5.0 Process Economics(3,7)

Capital and operating costs for electrostatic precipitators vary widely depending on the application. The range for installed costs has been \$7 to \$17 per actual m^3/hr (\$4 to \$10 per acfm). Operating costs range from \$0.08 to \$0.37 per actual m^3/hr (\$0.05 to \$0.22 per acfm). Based on these figures, the annualized costs would be about \$0.85 to \$3.40 per actual m^3/hr (\$0.50 to \$2.00 per acfm). These figures are based on 1974 dollars.

6.0 Input Streams - see Table D-32.

7.0 Discharge Streams

7.1 Gas Stream - see Table D-32

7.2 Particulates Collected - depends upon application

8.0 Data Gaps and Limitations

Electrostatic precipitators are used widely in numerous, and a range of industrial applications and considerable design and operating experience exist for existing applications. The design requirements for the application of the system to the purification of gases from coal conversion processes have not been evaluated. Such an evaluation would require

TABLE D-32. PERFORMANCE DATA - AN ELECTROSTATIC PRECIPITATOR(6)

Figures given as base on actual field data for one installation. The location of the installation, collection conditions, temperature, etc. are not reported.

Particle Diameter µm	Removal Efficiency %
0.2	95
0.4	94
0.6	95.5
1.0	97.3
2	99
4	99.4
6	99.4
8	99.5
10	99.5

data on the characteristics of the specific gas streams to be treated (e.g., particle size and size distribution, temperature, particle resistivity and presence of other constituents in the gas).

9.0 Related Programs

Research-Cottrell is presently involved in research on high temperature and pressure precipitators for use on coal conversion processes.

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3. Walker, A.B., Hot-Side Precipitators, JAPCA, 25:143, 1975.
4. Rao, A.K., et al, Particulate Removal From Gas Streams at High Temperature/High Pressure, EPA 600/2-75-020, August 1975.
5. McCain, J.D., et al, Results of Field Measurements of Industrial Particulate Sources and Electrostatic Precipitator Performance, JAPCA 25:117, 1977.
6. Lasater, R.C. and Hopkins, J.H., Removing Particulates from Stack Gases, Chemical Engineering, October 17, 1977.
7. McKenna, J.D. et al, Performance and Cost Comparisons Between Fabric Filters and Alternate Particulate Control Techniques, JAPCA, 24:1144, 1974.
8. Bush, J.R., Future Need and Impact on the Particulate Control Equipment Industry Due to Synthetic Fuels, presented at the 3rd Symposium on Environmental Aspects of Fuel Conversion Technology, Hollywood, Florida, September 1977.

VENTURI SCRUBBING PROCESS

1.0 General Information

1.1 Operating Principle - Physical removal of particulates from a gas stream by the inertial impactions of the particles with diffused scrubbant droplets.

1.2 Developmental Status - Commercially available.

1.3 Licensor/Developer - Many companies manufacture venturi scrubbing systems; each system incorporates certain proprietary features. A complete listing of manufacturers is presented in technical and trade journals (e.g., Ref. 1 and 2).

1.4 Commercial Applications - Venturi scrubbers have been applied to **foundry** cupolas, blast furnaces, lime kilns and a large number of miscellaneous industrial gas cleaning operations(3).

2.0 Process Information

2.1 Flow Diagram - see Figure D-20.

- Process Description - Particulate-laden gas stream (Stream 1) enters scrubber housing, passes through a venturi section through which low pressure water flows. The water is atomized by using some of the energy from the gas stream. Particles in the gas stream are moving faster than the atomized water; these particles are captured by the atomized water droplets by inertial impaction. The particulate-laden water is separated from the cleaned gas stream and sent to a water treatment facility and the cleaned gas is sent to further processing or ducted to a stack for release to the atmosphere.

2.2 Equipment - The scrubber housing and appropriate fittings and connections are part of the basic scrubber design; and are usually supplied by the manufacturer of the scrubbing device.

2.3 Feed Stream Requirements - Venturi scrubbing devices are applicable over wide ranges of temperature, pressure, and gas compositions;

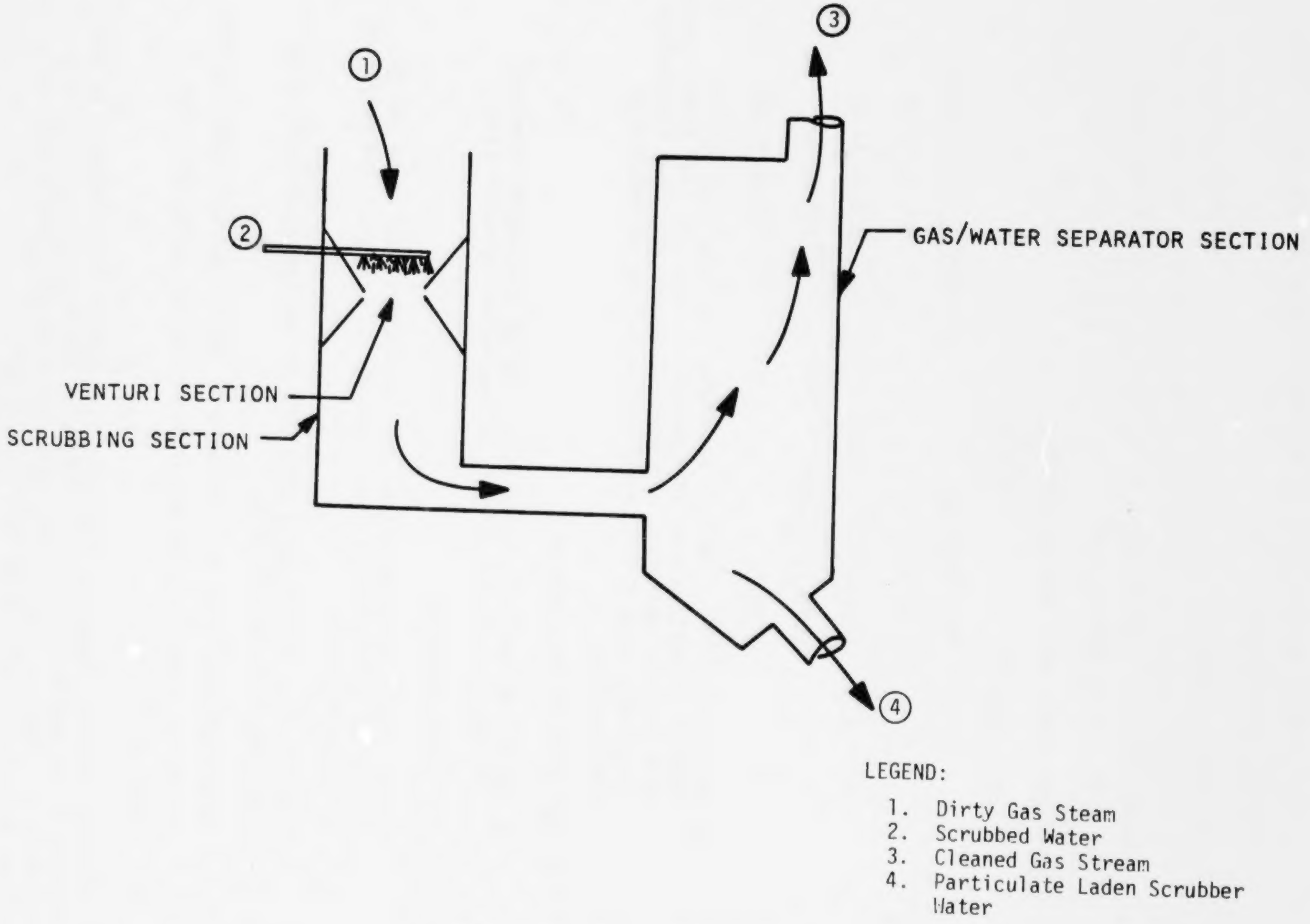
①
②
③
④
VENTURI SECTION
SCRUBBING SECTION
GAS/WATER SEPARATOR SECTION
LEGEND:
1. Dirty Gas Steam
2. Scrubbed Water
3. Cleaned Gas Stream
4. Particulate Laden Scrubber Water

Figure D-20. Venturi Scrubber

however, these devices must be designed to meet the specific needs of each application.

2.4 Operating Parameters (see Section 2.3 above) - The pressure drop across the venturi scrubbers varies depending upon the application; generally, the pressure drop is in the 2.4 kPa to 24 kPa range (10 in. H_2O to 100 in. H_2O).

2.5 Process Efficiency and Reliability*

- Efficiency(4)

Particle Mean Diameter	Control Efficiency
0.25μ	60% to 92.5%
0.50μ	85% to 97.2%
0.75μ	92% to 99%
1.00μ	95% to 99.6%

- Reliability(3,5) - Venturi scrubbers have been used for the removal of particulates from gaseous streams for over thirty years. When properly designed, operated and maintained, they can provide relatively trouble free service in a variety of industrial applications.

2.6 Raw Material Requirements

- Water treatment chemicals (e.g., for pH adjustment; chemical and design dependent on gas and raw water characteristics)

2.7 Utility Requirements

Water: quantity dependent on the particulate loading in the gas stream and whether provisions are made for treatment and recycling of the spent water.

Electricity: requirements dependent on the system pressure drop and water circulation ratio.

2.8 Miscellaneous - Care must be taken to correct pH adjustment to the scrubbing water to avoid excessive corrosion and/or plugging problems(6).

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*Reliability and efficiency are dependent on a number of parameters, primarily relating to the characteristics and changes in the characteristics of the gas stream (e.g., chemical composition, flow rate and particle size and distribution) and the scrubbing water (e.g., pH)(3,4,5)

3.0 Process Advantages(3,4,5,6)

- Effective performance over a wide loading range.
- Practically no re-entrainment of the particulates.

4.0 Process Limitation(4,5,6)

- High energy costs
- Difficulty of disposing of wet sludge
- Corrosion problems
- Possible visible moist plumes
- Scrubbing water is potential source of water pollution necessitating extensive water treatment facilities.

5.0 Process Economics - Installed cost

Installed [illegible]s for venturi scrubbers have been reported to vary from \$80.00 to \$170.[illegible]er normal cubic meter per min (\$2.11 to \$4.51 per acfm).* The operating costs (including the maintenance costs) are reported as \$30.00 to \$38.00 per normal cubic meter per min (10.76 - 10.96 per acfm) on an annulized basis(4).

6.0 Input Streams

- Input gas stream (Stream 1), see Table D-33.
- Scrubbing water (Stream 2), see Table D-33.

7.0 Discharge Stream

- Purified gas stream (Stream 3), see Table D-33.
- Particulate-laden water, Stream 4: (rate and composition dependent on particulate loading in the inlet gas stream, scrubber efficiency, and input water characteristics)

---

*The costs presented are in early 1974 dollars and for a 39,100 Nm^3/hr (70,000 acfm) unit operating at 395°K (250°F) with scrubber efficiencies of 97% and 99%, respectively.

TABLE D-33. SOME TYPICAL APPLICATIONS OF VENTURI SCRUBBERS WITH APPROPRIATE GAS AND LIQUID STREAM INFORMATION(3)

Application	Saturated Gas		Throat Gas Velocity m/s (ft/sec)	Liquid Flow Rate Stream 2 gpm/min	Dust Concentration gm/Nm^3 (gr/scf)		Pressure Drop kPa (inches H_2O)
	Flow Rate Nm^3/m (acfm)	Temperature °K (°F)			In Stream 1	Out Stream 3	
Black Liquor recovery boiler	5,000 (185,000)	354 (177)	61 (200)	10500 (2775)	6.7 (3)	0.11 (0.05)	8.4 (35)
Fly Ash Sinter Furnace	1,600 (60,000)	314 (105)	32 (105)	1360 (360)	1.36 (0.61)	0.11 (0.05)	1.2 (5)
Blast Furnace	6,100 (225,000)	330 (135)	110 (360)	12000 (3150)	8.9 (4)	0.01 (0.005)	14.4 (60)
Foundry Cupola	1,100 (41,400)	327 (130)	107 (350)	2650 (700)	17.9 (8)	0.07 (0.03)	13.2 (55)

8.0 Data Gaps and Limitations

Extensive performance data are available for venturi scrubber applications to a variety of industrial gas cleaning operations. Evaluation of expected performance of the system in applications to coal gasification plant gas streams (e.g., coal and ash lock hopper vent gases) requires data on chemical characteristics of the gas and the particle size distribution of the particulates to be removed.

REFERENCES

1. Produce Guide, Journal of the Air Pollution Control Association, Vol. 27, No. 3, 1977.

2. Environmental Control Issue, Control Equipment, Environmental Science and Technology, October 1977.

3. Hesketh, H.E., Fine Particle Collection Efficiency Related to Pressure Drop, Scrubbant and Particle Properties and Contact Mechanisms; Journal of the Air Pollution Control Association, Vol. 24, No. 10, 1974.

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5. Ekman, F.O. and Johnstone, H.F., Collection of Aerosols in a Venturi Scrubber; Industrial and Engineering Chemistry, Vol. 43, No. 6, June 1951.

6. Striner, B.A. and Thompson, R.J., Wet Scrubber Experience for Steel Mill Applications, JAPCA, Vol. 27, No. 11, 1977.

CYCLONES

1.0 General Information

1.1 Operating Principles - Removal of particulates from a gas stream by the action of centrifugal forces.

1.2 Developmental Status - Commercially available.

1.3 Licensor/Developer - Many companies manufacture cyclone collectors. Listings of manufacturers are contained in various trade and technical journals (e.g., Ref. 1).

1.4 Commercial Application - Widely used in the chemical process industry for removal of particulates from gaseous streams; also used as a final collection device before gas discharge where particles are large or loading light. Frequently used as a precleaner before more efficient control devices.

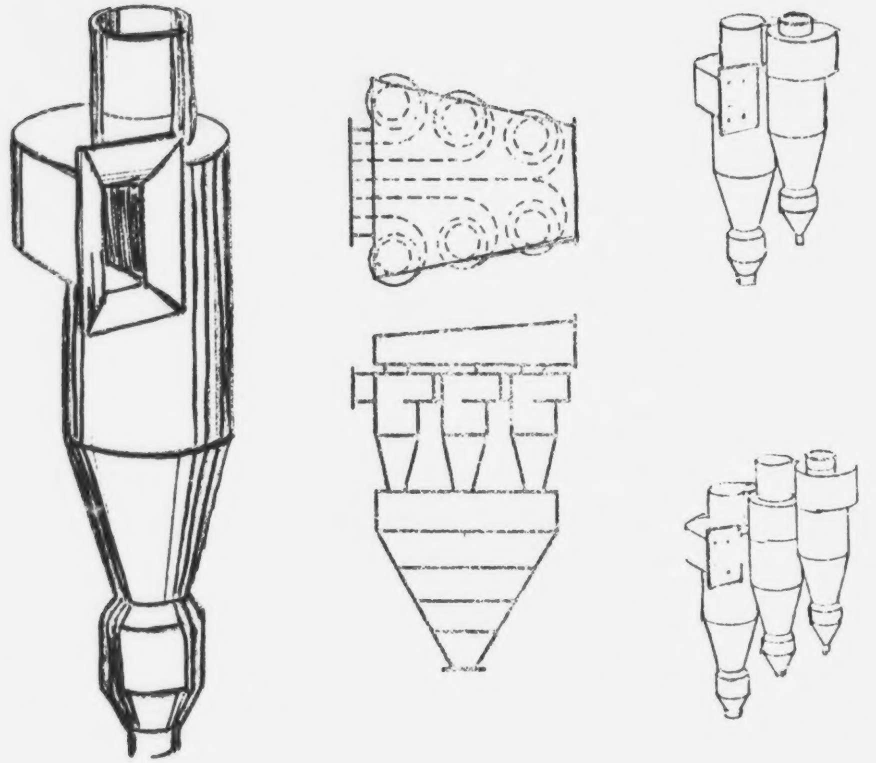
2.0 Process Information

2.1 Flow Diagram - see Figure D-21

- Process Description - Cyclones operate by imparting a centrifugal force to the gas stream. The circular shape and tangential entrance change the gas flow pattern to a vortex, spiraling it downward. The inertia of the particles carries them to the cyclone wall and down the sides to a collector section from which they are removed(3).

2.2 Equipment - Cyclones can be either single or multiple; multiple units can be arranged in either series or parallel (see Figure D-21).

- Construction - May be constructed from any suitable material. Primary considerations are: temperature, pressure, abrasiveness and corrosive tendencies of the gas or particulate matter.



Single Tube

Multiple Tube
Parallel
Arrangement

Multiple Tube
Series
Arrangement

Figure D-21. Cyclone - Illustrating Single and Multiple Tube Arrangements for Parallel or Series Operation(2)

2.3 Feed Stream Requirements

- Temperature - Relatively unaffected by temperature(4); construction materials and methods must take temperature into account.
- Pressure - Relatively unaffected by pressure(4); construction materials and methods must take pressure into account.
- Particle Size and Composition - Cyclones are generally limited to applications where particle size is about 5 μm. Multi-cyclone units with high pressure drop have been applied for removal of particles down to 3 μm.

2.4 Process Efficiency and Reliability(4) - Efficiency is dependent on: particle size and density, loading, inlet velocity, cyclone dimensions and the gas density and viscosity. The general range of efficiencies are:

Particle Size, μm	Range of Efficiency, %
5 μm	50 to 80
5 to 20 μm	80 to 95

Reliability is high due to a simple system with no moving parts. Some problems with removal of collected particulates (in coal gasification gasifiers) has been reported(5).

2.5 Raw Material Requirements - none

2.6 Utility Requirements

- Electricity - To overcome the pressure drop across the system (to power fan or blower).

2.7 Miscellaneous - Maintenance requirements are very low due to a simple system with no moving parts.

3.0 Process Advantages

- Mechanically simple
- Highly reliable
- Relatively small space requirements
- Can handle hot, high pressure gas streams with little change in efficiency

- Low cost
- Low energy consumption

4.0 Process Limitations

- Inability to collect small particles (below 5 μm)
- Large gas flows require multiple units

5.0 Process Economics

Due to the wide variety of applications, sizes, materials of construction and types of cyclones in use, no generalized cost figures are available.

6.0 Input Streams

Due to the many variables involved in determining cyclone performance, a generalized figure is presented (Figure D-22). Efficiency is plotted against particle size for various pressure drops. The figure shows the rapid deterioration of efficiency as particle size decreases. The figure also shows the increase in efficiency with increased pressure drop.

7.0 Discharge Streams - see Figure D-22.

8.0 Data Gaps and Limitations

The performance of cyclones can be accurately predicted once particulate and gas stream parameters are known. Characterization, with respect to these parameters, of coal gasification streams is needed to determine applicability and performance for specific cases.

9.0 Related Programs - Not applicable.

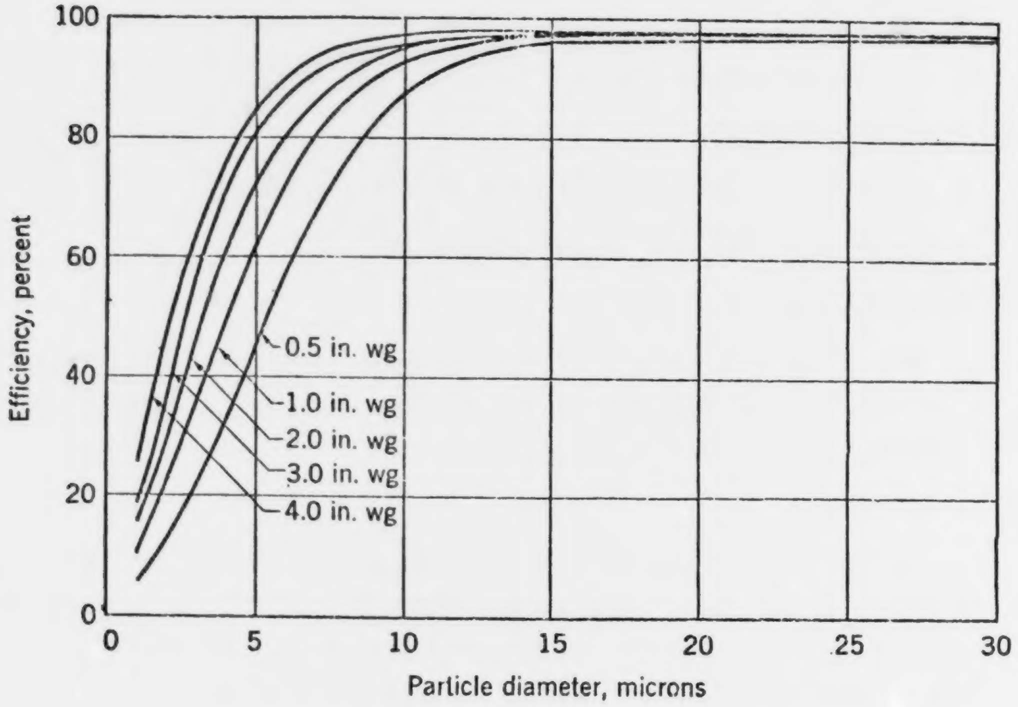


Figure D-22. Cyclone Efficiency vs. Particle Size and Pressure Drop(2)

REFERENCES

1. Product Guide, JAPCA, Vol. 27, No. 3, 1977.

2. Walker, A.B., Operating Principles of Air Pollution Control Equipment: Guidelines for Their Application, Research-Cottrell.

3. Hesketh, H.E. Understanding and Controlling Air Pollution, Ann Arbor Science Publishers Inc., 1973.

4. Lasater, R.C. and Hopkins, J.H., Removing Particulates from Stack Gases, Chemical Engineering, October 17, 1977.

5. Haynes, W.P., et al, Synthane Process Update, Mid-77, presented at the 4th Annual Conference on Coal Gasification, Liquefaction and Conversion to Electricity, University of Pittsburg, August 2-4, 1977.

Hydrocarbon and Carbon Monoxide Control Module

Thermal Oxidation

Catalytic Oxidation

Activated Carbon Adsorption (see Methanation Guard Module, Appendix B)

THERMAL OXIDATION PROCESS
(Direct-Flame Afterburners)

1.0 General Information

1.1 Operating Principle - The oxidation of combustible compounds (e.g. hydrocarbons, CO, H_2S) from many types of industrial waste gas streams by direct combustion. In practice, thermal oxidizers are generally used for the destruction of residual combustibles after bulk of such materials is removed by prior treatment (e.g., by conventional incineration). The typically low concentration of combustibles in such waste gases usually requires that supplemental fuel be used.

1.2 Development Status - Commercially available.

1.3 Licensor/Developer - Many companies manufacture direct-flame afterburners; some systems incorporate certain proprietary features. A complete listing of manufacturers are presented in technical and trade journals (e.g. Reference 1).

1.4 Commercial Applications - Widely used in various industrial applications to control odors, smoke, total hydrocarbons and carbon monoxide(2). Potential applications of thermal oxidation in a coal gasification facility may be in connection with emission control from lock hoppers, Claus plant and regeneration of process catalysts.

2.0 Process Information

2.1 Flow Diagram - see Figure D-23.

- Process Description: The contaminated gas (Stream 1) enters the unit, passes through the burner flames in the upstream part of the unit. The hot gaseous mixture then passes through the remaining part of the chamber where the combustion process is complete, prior to being discharged to the atmosphere.

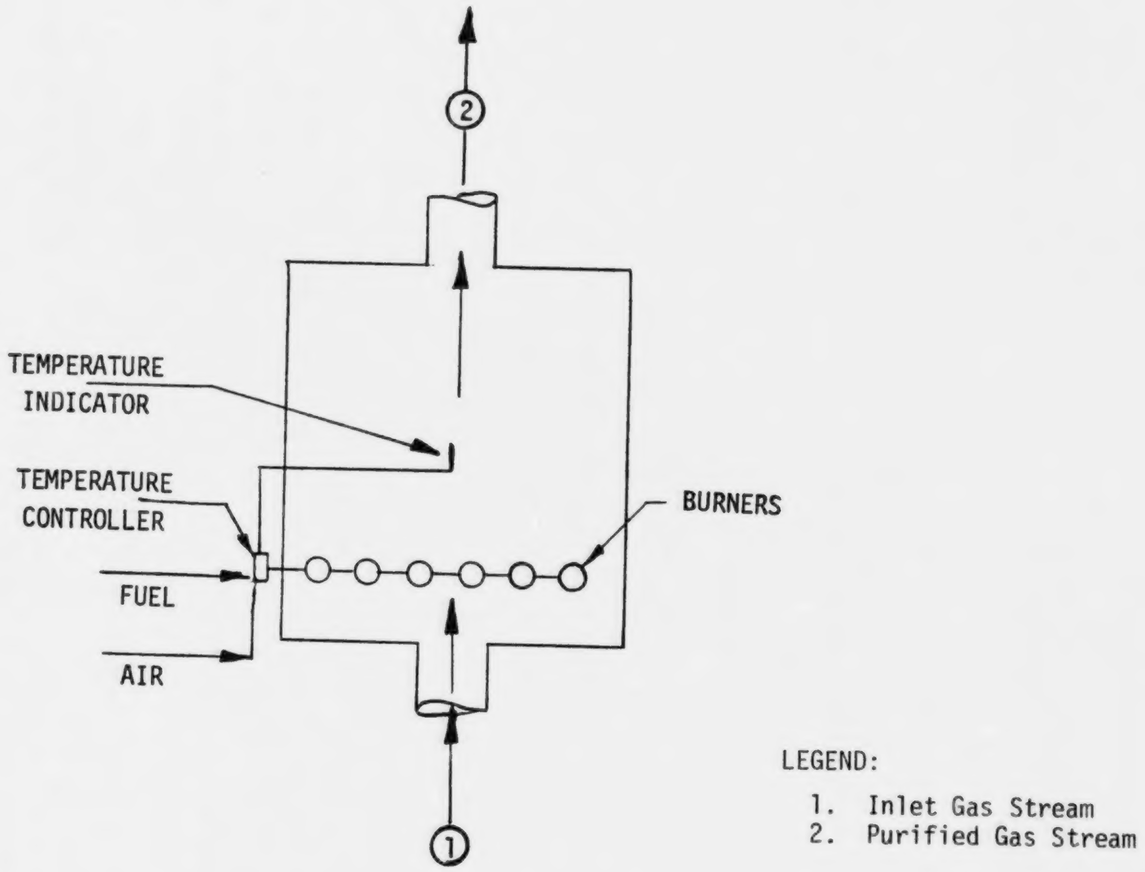

2
TEMPERATURE INDICATOR
TEMPERATURE CONTROLLER
BURNERS
FUEL
AIR
1
LEGEND:
1. Inlet Gas Stream
2. Purified Gas Stream

Figure D-23. Direct-Fired Afterburner (Thermal Oxidation)

2.2 Equipment - Conventional refractory-lined chamber, one or more burners, temperature indicator-controllers.

2.3 Feed Stream Requirements

- Temperature: The inlet gas at any temperature can generally be handled; however, the lower the temperature, the greater would be the requirements for preheating and hence the supplementary fuel requirements.
- Pressure: No limitation.
- Gas Composition: Many waste gas streams containing a wide variety of combustible materials can be treated with thermal oxidation.

2.4 Operating Parameters(2)

2.4.1 Combustion Chamber*

- Temperature: 839°K to 1005°K (1050°F to 1350°F)†; 1005°K to 1089°K (1350°F to 1500°F)‡
- Pressure drop: 1.2 to 4.9 cPa (0.5 in. to 2.0 in. water)
- Residence time: 0.3 to 1.0 second
- Superficial velocity: 1.23 to 15.25 meters/sec (4 to 5 afps)

2.5 Process Efficiency and Reliability - Through the control of temperature (supplemental fuel and air addition), different levels of combustion efficiency can be achieved in response to changes in inlet gas characteristics. In typical applications, 90% reduction of hydrocarbons can be achieved. Years of operation have proven the system reliable and efficient(2).

2.6 Raw Material Requirements - None.

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*Basis: 90% elimination of carbonaceous material from gas stream as determined by the following equation for operating efficiency:

$$\frac{\text{Hydrocarbons In} - [\text{Hydrocarbons Out} + (\text{CO out} - \text{CO in})]}{\text{Hydrocarbons In}} \times 100$$

†Approximate temperature requirements for hydrocarbon control.
‡Approximate temperature requirement of hydrocarbon and CO control.

2.7 Utility Requirements

- Fuel - Fuel requirements vary as a function of the type of fuel used, inlet gas stream temperature and the amount of combustibles present in the gas stream. Table D-34 gives some typical fuel requirements.

2.8 Miscellaneous - No unusual maintenance or hazardous conditions are reported.

TABLE D-34. SUPPLEMENTAL FUEL REQUIREMENT FOR DIRECT-FIRED OXIDIZER AS A FUNCTION OF RAW GAS TEMPERATURE AND HYDROCARBON CONCENTRATIONS (AS HEXANE)*(5)

Natural Gas as Fuel	Volume/hr of fuel to volume/min waste gas			
Conc. of Hydrocarbons, ppm	0	1000	2000	3000
Raw Gas Temperature, °K (°F)				
311°K (100°F)	2.6	2.18	1.73	1.3
366°K (200°F)	2.42	2.0	1.58	1.18
477°K (400°F)	2.22	1.62	1.22	0.8
589°K (600°F)	1.61	1.21	0.81	0.04
700°K (800°F)	1.22	0.81	0.41	--
Oil as Fuel	Liters of oil per hour per 100 Nm^3 per minute waste gas (GPH/MSCFH waste gas)			
Conc. of Hydrocarbon, ppm	0	1000	2000	3000
Raw Gas Temperature, °K (°F)				
311°K (100°F)	16.7 (17)	13.7 (14)	13.2 (13.5)	8.5 (8.7)
366°K (200°F)	15.7 (16)	12.7 (13)	9.8 (10)	7.4 (7.5)
477°K (400°F)	13.0 (13.3)	10.3 (10.5)	7.8 (8)	4.9 (5)
589°K (600°F)	10.8 (11)	8.0 (8.2)	5.4 (5.5)	2.3 (2.4)
700°K (800°F)	8.3 (8.3)	3.2 (3.3)	2.9 (3)	---

*Assumes an oxidizer operating temperature of 1033°K (1400°F).

3.0 Process Advantages

- Process has been successfully used for years as an air pollution control device to reduce hydrocarbons and various other combustible contaminants from gas streams.
- May be easily installed as a retro-fit to existing installations.
- The performance of the system does not deteriorate with time.
- There is only one control point variable, chamber temperature. The temperature and hence the process efficiency is readily controlled by varying the fuel flow rate.

4.0 Process Limitations

- Requires supplemental fuel to raise raw gas temperature(2,3).
- Will not oxidize/remove contaminants which are already in oxidized form (e.g., SO_2, SO_3)(2).
- Oxidation or partial oxidation of contaminants containing halogens may create extremely hazardous effluent (e.g., hydrogen chloride, phosgene)(2).
- At lower operating temperatures, only partial oxidation of organics may be achieved and the decrease in organics concentration may be accompanied by an increase in the CO level. When the generation of CO is considered in the determination of the system efficiency,* the efficiency of a direct-fixed boiler is usually less than 90% at operating temperatures below 477°K (1300°F)(3).

5.0 Process Economics(4)

Typical costs of a direct flame unit is as follows:

Equipment - \$15.00 to \$30.00 per 100 Nm^3/min (\$5.00 to \$10.00/scfm)

Fuel - \$0.00 to \$80.00 per 100 Nm^3/min per year (\$0.00 to \$20.00 per 1000 scfm per year)

6.0 Input Streams

6.1 Feed Gas Stream (see Figure D-23, Stream 1) - This stream generally contains hydrocarbons, CO, CO_2, and possibly small amounts of H_2S, SO_2, COS and various trace elements. The stream may be a discharge

---

$$^*\text{Efficiency} = \frac{\text{Hydrocarbons in} - [\text{hydrocarbons out} + (\text{CO out} - \text{CO in})]}{\text{Hydrocarbons in}} \times 100$$

stream from sulfur recovery plant tail gas treatment plants or other air pollution abatement equipment.

6.2 Fuel - Quantities required depend on raw gas temperature, operating efficiency desired and type of fuel used (see Table D-34.

7.0 Discharge Streams

7.1 Purified Gas Stream (see Figure D-23, Stream 2) - This stream will contain primarily CO_2, H_2O and N_2 with small amounts of SO_x, NO_x and traces of hydrocarbons and particulate matter.

8.0 Data Gaps and Limitations

Extensive performance data are available for direct-fired oxidation applications to a variety of industrial gas cleaning operations. Evaluation of expected performance of the system in applications to coal gasification plant waste gas streams requires data on detailed characterization of the gas to be treated. Such data which include gas temperature, and chemical characteristics including a trace element survey, are generally currently either not available or are incomplete.

9.0 Related Programs - No available data.

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4. Hesketh, H.E., Understanding and Controlling Air Pollution, Ann Arbor Science Publishers, Inc., 1972.
5. Rolke, R.W., et al, Afterburner System Study. Report No. EPA-R2-72-062, NTIS No. PB-212 560, EPA Contract No. EHS-D-71-3, Emeryville, California, Shell Development Co., August 1972.

CATALYTIC OXIDATION PROCESS

1.0 General Information

1.1 Operating Principles - The oxidation of combustible compounds (e.g. hydrocarbons, CO, H_2S) in a gas stream by passing the gas stream through a catalyst bed. The catalysts most commonly used are precious metals (e.g., platinum and palladium) supported on various carrier materials (e.g. alumina, nickel). Various other catalysts (e.g. metallic oxides, copper chromite) can also be used. In practice, catalytic oxidizers are generally used for the destruction of residual pollutants in a gas stream, after bulk of such pollutants are removed by prior treatment (e.g., thermal oxidation or conventional incineration). Use of supplementary fuel is usually required.

1.2 Development Status - Commercially available.

1.3 Licensor/Developer - Many companies manufacture catalytic oxidation systems; most systems generally incorporate certain proprietary features and catalytic formulation. A listing of major manufacturers are presented in technical and trade journals (e.g., Reference 1).

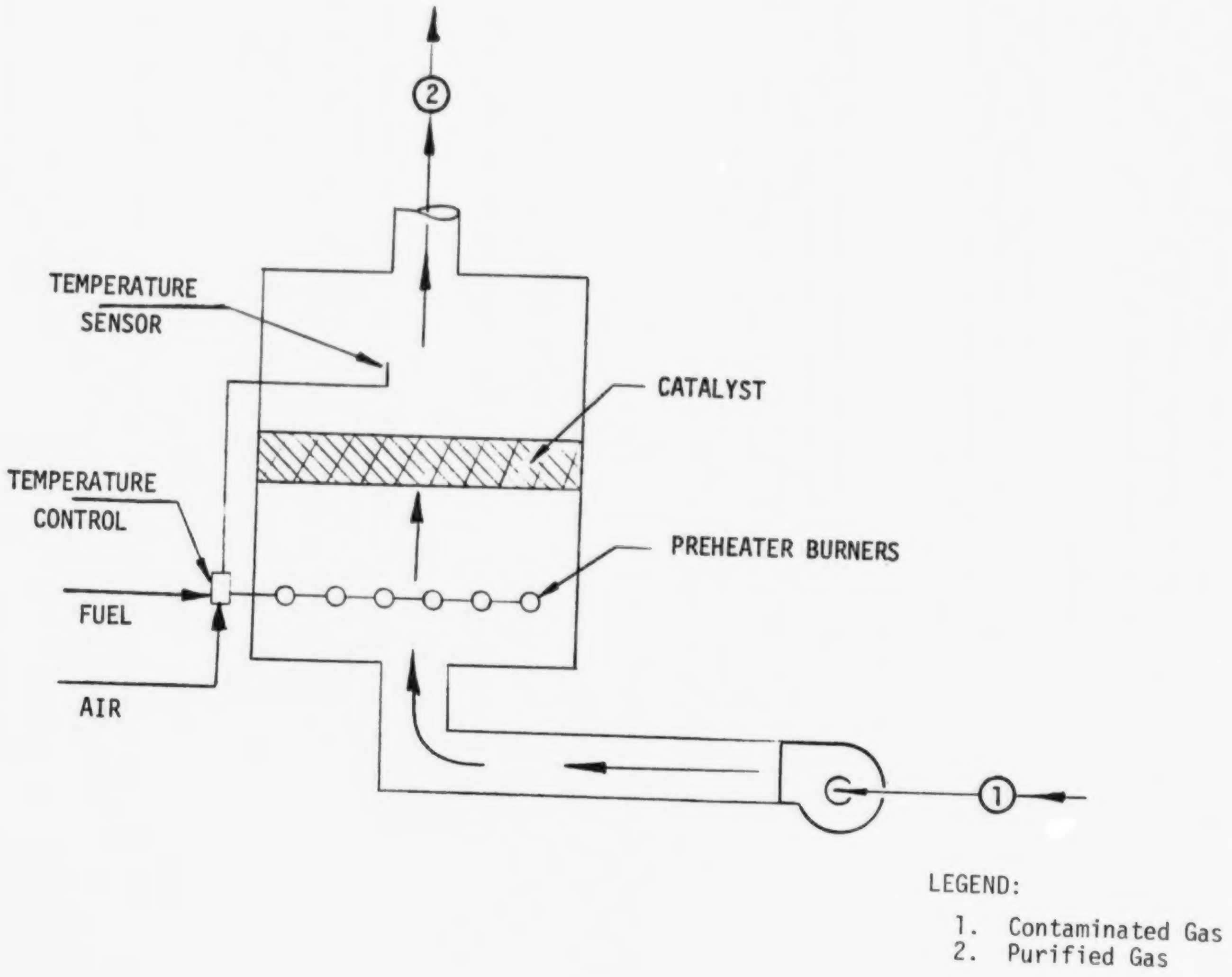
1.4 Commercial Applications - Catalytic oxidation units have been applied to coke ovens, catalytic cracking units, and a large number of miscellaneous industrial gas cleaning operations(2). Potential applications of catalytic oxidation in a coal gasification plant may be in connection with the control of emissions from lockhoppers, Claus plant and regeneration of process catalysts.

2.0 Process Information

2.1 Flow Diagram - see Figure D-24

- Process Description: The contaminated gas, Stream 1, is blown into a preheat zone, where it is heated to the required temperature. The gas then flows through the catalytic element. The

Figure D-24. Catalytic Oxidation



②
TEMPERATURE SENSOR
CATALYST
TEMPERATURE CONTROL
PREHEATER BURNERS
FUEL
AIR
①
LEGEND:
1. Contaminated Gas
2. Purified Gas

purified gas, Stream 2, exits the unit and can be released directly to the atmosphere, or sent on for further treatment and heat recovery(3).

2.2 Equipment - Conventional refractory-lined chamber, one or more burners, catalyst chamber, and where applicable, heat recovery equipment, temperature indicator-controller(3).

2.3 Feed Stream Requirements

- Temperature: The inlet gas at any temperature can generally be handled; however, the lower the inlet gas temperature, the greater would be the requirements for preheating and hence the supplementary fuel requirements.
- Pressure: None.
- Gas Composition: Many waste gas streams containing a wide variety of oxidizable material can be treated by catalytic oxidation; however, the presence of heavy metals (e.g., mercury, lead, arsenic), certain sulfur compounds, resin solids and particulates in the gas stream can seriously effect the performance of the system due to plugging and/or poisoning of the catalyst(3).

2.4 Operating Parameters(3,4)

2.4.1 Preheat Chamber

- Temperature: 589°K to 811°K (600°F to 1000°F)
- Pressure: 0.1 to 13.7 MPa (atmospheric to 2000 psig)

2.4.2 Catalytic Chamber

- Temperature: For many applications, the temperature is 111°K (200°F) higher than the preheat chamber due to exothermic chemical reactions occurring in the catalyst bed.
- Pressure: Approximately the same as in the preheat chamber; any difference is due to pressure drop across catalyst bed.

2.5 Process Efficiency and Reliability

- The efficiency of a catalytic oxidizer is a function of several variables including(3):
  - operating temperature of the unit
  - type of catalyst being used, including surface area, bed depth, amount of catalyst to volume of gas being treated.

  - nature of contaminants to be oxidized
  - uniformity of gas flow through catalyst bed

- Catalytic oxidizing units can be selected and/or designed to remove 90% or more of the oxidizable materials from most gas streams(2).

- With proper catalyst maintenance and replacement the system will continuously meet efficiency requirements.

2.6 Raw Material Requirements

- Catalyst makeup: Depending upon the type of catalyst used, gas stream components, and flow rate, the interval between catalyst replacement can vary from a few months to as long as two years(3).

2.7 Utility Requirements

- Fuel: Fuel requirements vary as a function of the type of fuel used, inlet gas stream temperature and the amount of oxidizable chemicals present in the gas stream . Table D-35 gives some typical fuel requirements.

2.8 Miscellaneous - Depending on the nature of the contaminants present in the inlet gas stream, frequent changing of the catalyst may be required particularly if catalyst poisons (arsenic, mercury, tars, etc.) are present in the inlet stream. The handling and disposal of the spent catalyst may require special attention because it may be contaminated with various toxic substances, such as heavy metals.

3.0 Process Advantages

- Catalytic oxidation is particularly suitable for removing small amounts of oxidizable contaminants.

- The system can be readily applied (either by incorporation in original design or by retrofit) to a variety of industrial applications as an an air pollution abatement device(5).

- Lower supplemental fuel requirements than conventional thermal oxidizers(6).

TABLE D-35. SUPPLEMENTAL FUEL REQUIREMENTS FOR CATALYTIC OXIDIZERS AS A FUNCTION OF RAW GAS TEMPERATURE AND HYDROCARBON CONCENTRATIONS (AS HEXANE)*(8)

Natural Gas as Fuel	Volume/hr fuel to volume/min waste gas			
Conc. of Hydrocarbons, ppm	0	1000	2000	3000
Raw Gas Temperature, °K (°F)				
311°K (100°F)	1.3	0.95	0.55	0.2
366°K (200°F)	1.19	0.80	0.45	--
377°K (400°F	0.90	0.48	--	--
589°F (600°F)	0.53	--	--	--
Oil as Fuel	Liters of oil per hour per 100 Nm^3 per minute waste gas (gph fuel/Mscfh waste gas)			
Conc. of Hydrocarbons, ppm	0	1000	2000	3000
Raw Gas Temperature, °K (°F)				
311°K (100°F)	8.3 (8.5)	6.1 (6.2)	3.7 (3.8)	1.4 (1.5)
366°K (200°F)	7.3 (7.4)	5.1 (5.2)	2.7 (2.8)	0.5 (0.5)
477°K (400°F)	5.6 (5.7)	3.0 (3.1)	--	--
589°K (600°F)	3.4 (3.5)	--	--	--

*Assumes a gas exit temperature of 775°K (900°F).

4.0 Process Limitations

- The efficiency of a catalytic oxidation unit deteriorates with use, due to catalyst degradation caused by age and contamination(3).
- The catalyst must be periodically changed; the spent catalyst (which may contain hazardous substances) must be handled and a suitable means of disposal must be used(2,4,5)
- The products of the catalytic oxidation process may still constitute an air pollution problem (e.g., $H_2S + O_2 = H_2O + SO_x$)(4).
- Catalysts are susceptible to poisoning and/or fouling by heavy metals, sulfur oxides and resin solids(3).

5.0 Process Economics(7)

Typical costs of a catalytic oxidation unit are as follows:

Equipment - \$5.00 to \$15.00 per 100 Nm^3/m (\$1.75 to \$5.00 per scfm)

Fuel - \$0.00 to \$18.00 per 100 Nm^3/m per year (\$0.00 to \$4.50/1000 scfm per year)

6.0 Input Streams

6.1 Feed Gas Stream (see Figure D-24, Stream 1). This stream is generally made up of hydrocarbons, CO, CO_2, H_2, and possibly small amounts of H_2S, SO_2, COS, and various trace elements. This stream may be the tail gas stream from a sulfur recovery plant, a tail gas treatment plant or other air pollution abatement equipment.

6.2 Catlyst replacement/makeup - Depends on the nature of catalyst and operating conditions.

7.0 Discharge Streams

7.1 Purified gas stream (see Figure D-24, Stream 2) - This stream will contain primarily CO_2, H_2O and N_2 with small amounts of SO_x, NO_x and traces of hydrocarbons and particulate matter.

7.2 Spent catalyst - no data available.

8.0 Data Gaps and Limitations

Extensive performance data are available for catalytic oxidation applications to a variety of industrial gas cleaning operations. Evaluation of expected performance of the system in applications to coal gasification plant waste gas streams requires data on detailed characteristics of the gas to be treated. Such data which include gas temperature, and chemical characteristics including a trace element survey are generally either not available or are incomplete.

9.0 Related Programs - No available data.

REFERENCES

1. Environmental Control Issue, Control Equipment, Environmental Science and Technology, October 1977.
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APPENDIX E

WATER POLLUTION CONTROL

Oil and Suspended Solids Removal Module

Gravity Separation (API Separators)
Flotation
Filtration
Coagulation-Flocculation

GRAVITY SEPARATION (API SEPARATORS) PROCESS

1.0 General Information

1.1 Operating Principles - Free oil is separated from a wastewater by retaining the wastewater in a basin where the oil globules (having a lower density than water) rise to the surface under the influence of gravity and are collected at the surface. Particles denser than water which may settle to the bottom are collected as bottom sludge.

1.2 Development Status - Oily water separators have been used industrially for decades to recover oil from process waste streams.

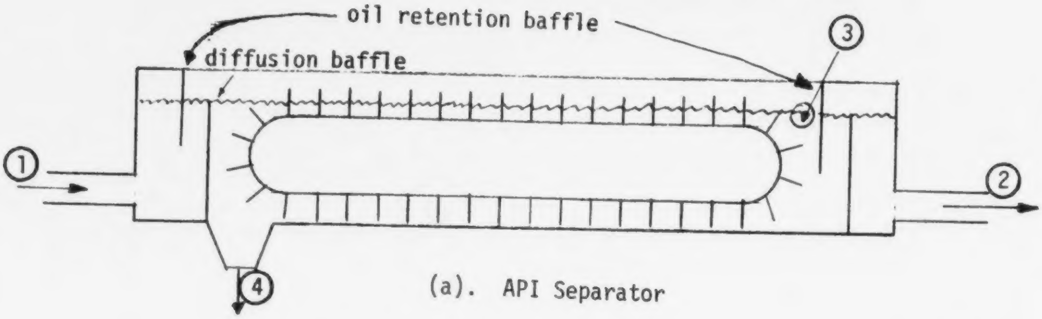
1.3 Licensor/Developer - The American Petroleum Institute has developed guidelines for design of rectangular shaped gravity separators (known as API separators). API and other types of separators, especially the smaller parallel plate separators, are offered by a number of water pollution control equipment suppliers.

1.4 Commercial Applications - Widely employed in refineries for removal of oil and suspended solids.

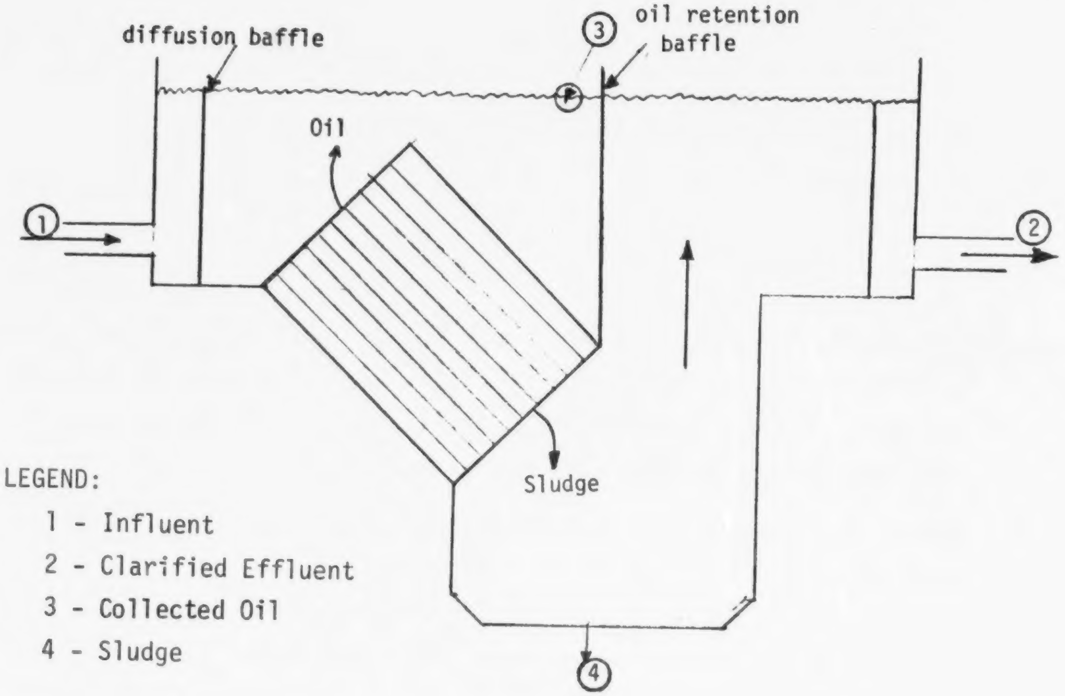
2.0 Process Information

Three of the most common types of gravity separators are the API, circular and parallel plate separators.

- The API Separator [Figure E-1(a)] - The wastewater enters the basin and passes under the oil retention baffle, then over the diffusion baffle (to minimize turbulence). As the wastewater travels the length of the channel, the oil globules move toward the surface and the heavy particles settle downward. Flight scrappers push the oil which has reached the surface towards one end and into the slotted pipe for removal. At the same time the flight scrappers push sludge deposits on the bottom of the basin to sludge hoppers. Clarified water passes under the oil retention baffle No. 2 and leaves the unit.


oil retention baffle
diffusion baffle
③
①
②
④

(a). API Separator


diffusion baffle
③
oil retention baffle
Oil
①
②
Sludge
LEGEND:
1 - Influent
2 - Clarified Effluent
3 - Collected Oil
4 - Sludge
④

(b). Parallel Plate Separator

Figure E-1. Gravity Separators

- Circular Separators (not shown) - In general, these types of separators are designed similar to the conventional circular clarifier. In most designs, influent enters at a central location in the circular tank and has a peripheral discharge(1). Pilot plant studies indicate that circular units may be as effective as an API separator(1,5).

- Parallel Plate (or tube) Separators [Figure E-1(b)] - The wastewater enters the separator and flows over a weir and through the parallel plates (or tubes). The plates can either be corrogated or flat. The oil particles coalesce on the under side of the plates and rise up to the surface where they are removed. Solids collect on the bottom of the plates and slide downward towards the sludge hopper for removal.

2.1 Equipment

- Separation tank - Concrete, tile or coated steel. The design criteria for rectangular API type separators are as follows(2):
  - Horizontal velocity (V_H) maximum = 0.91 m/min (3 ft/min) or 15 V_t (V_t* = rate of rise of oil) whichever is smaller.
- Depth = 0.9 m (3 ft) minimum to 2.44 m (8 ft) maximum
- Depth-to-width ratio - 0.3 minimum to 0.5 maximum
- Width = 6 ft minimum to 20 ft maximum

2.2 Feed Stream Requirements - Due to large variation in wastewater characteristics (e.g., specific gravity of oil, concentration of settleable solids, temperature of feed stream, presence or absence of emulsions) design of the separator is "tailored" to the specific wastewater to be treated (V_t determined in laboratory tests)(2).

2.3 Operating Parameters - Operating parameters are variable because each separator is designed to handle a specific influent. The vertical rate of rise of the oil globules (V_t) ideally will be equal to the overflow rates(2). In most cases, however, turbulence and short circuiting affect the efficiency of oil removal. Ideally, as long as V_t is greater than the overflow rate oil will be removed and not carried out in the clarified effluent.

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* $V_t = 0.0241 \left(\frac{S_w - S_o}{N}\right)$ where V_t = rate of rise of oil globules (0.015 cm in diameter) in wastewater, in fpm; S_w and S_o = specific gravity of water and oil in wastewater at design temperature, respectively; and N = absolute viscosity of wastewater at design temperature, in poises.

2.4 Process Efficiency and Reliability - Typical efficiencies of various oil separation units and parallel plate separators are shown in Tables E-1 and E-2. API separators are widely used in the petroleum refining industry; the system has proved effective and reliable for separation of oil from wastewaters.

2.5 Raw Material Requirements - None.

2.6 Utility Requirements

- Electricity(6) - 14.9 kwh/1000 gal

3.0 Process Advantages(5)

- General
  - Economical(5)
  - Simple Operation(5)
- Parallel Plate Separator
  - 15%-20% of the installation area of regular separators(5)
  - Removal efficiencies generally higher than for regular separators(3) (see Figure E-2)

4.0 Process Limitations

- Removal efficiency decreases as the wastewater temperature drops
- Removes little or no soluble and emulsified oils(5)
- API type separators are designed to affect complete removal of oil globules with diameters equal to or greater than 0.015 cm (0.006 in.); smaller particles would be removed only fractionally.
- Peak flow rates may decrease removal efficiency due to rise in the overflow rates (see Figure E-3)

5.0 Process Economics

Capital cost for a 3,780 l/min (1000 gal/min) capacity gravity separator for treatment of oily wastewaters depends largely on the desired effluent oil concentration (see Figure E-4). Operating cost

TABLE E-1. TYPICAL EFFICIENCIES OF OIL SEPARATION UNITS[3]

Oil Content					
Influent, mg/l	Effluent, mg/l	Oil % Removed	Type of Separator	CCD % Removed	SS % Removed
300	40	87	Parallel plate	--	--
220	49	78	API	45	--
108	20	82	Circular	--	--
108	50	54	Circular	16	--
98	44	55	API	--	--
100	40	60	API	--	--
42	20	52	API	--	--
2,000	746	63	API	22	33
1,250	170	87	API	--	68
1,400	270	81	API	--	35

TABLE E-2. OIL REMOVAL, TILTED-PLATE SEPARATOR[3]

Oily Water Throughput l/hr (gal/hr)	Influent Oil mg/l	Effluent Oil mg/l	Percent Removal
2100 (8000)	150	50	67
2100 (8000)	375	66	82
2100 (8000)	500	86	83
4200 (16,000)	500	178	65
4800 (16,000)	500	190	62
4800 (18,600)	470	185	67
4800 (18,600)	700	330	53

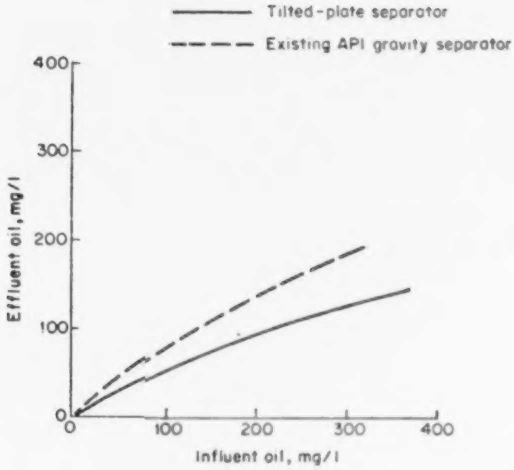

Figure E-2. Removal Efficiency of Pilot-Scale Titled-Plate Separator Compared to Full-Scale API Separator(3)

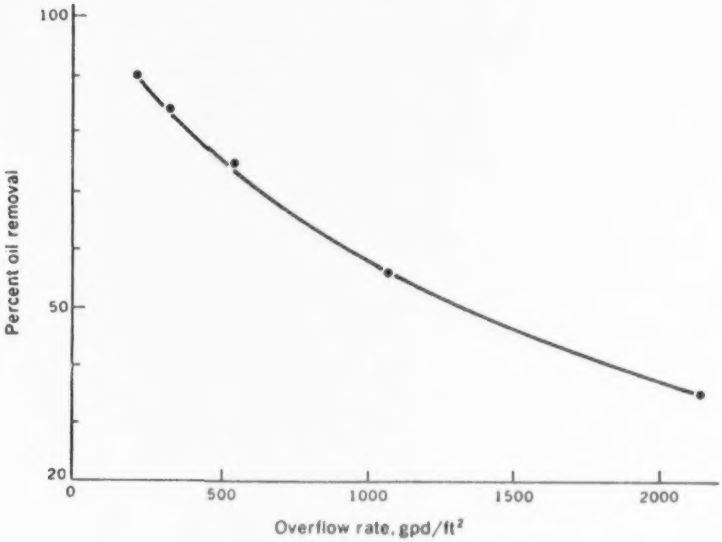

Figure E-3. Efficiency of Oil Removal from a Baffled Separator(4)

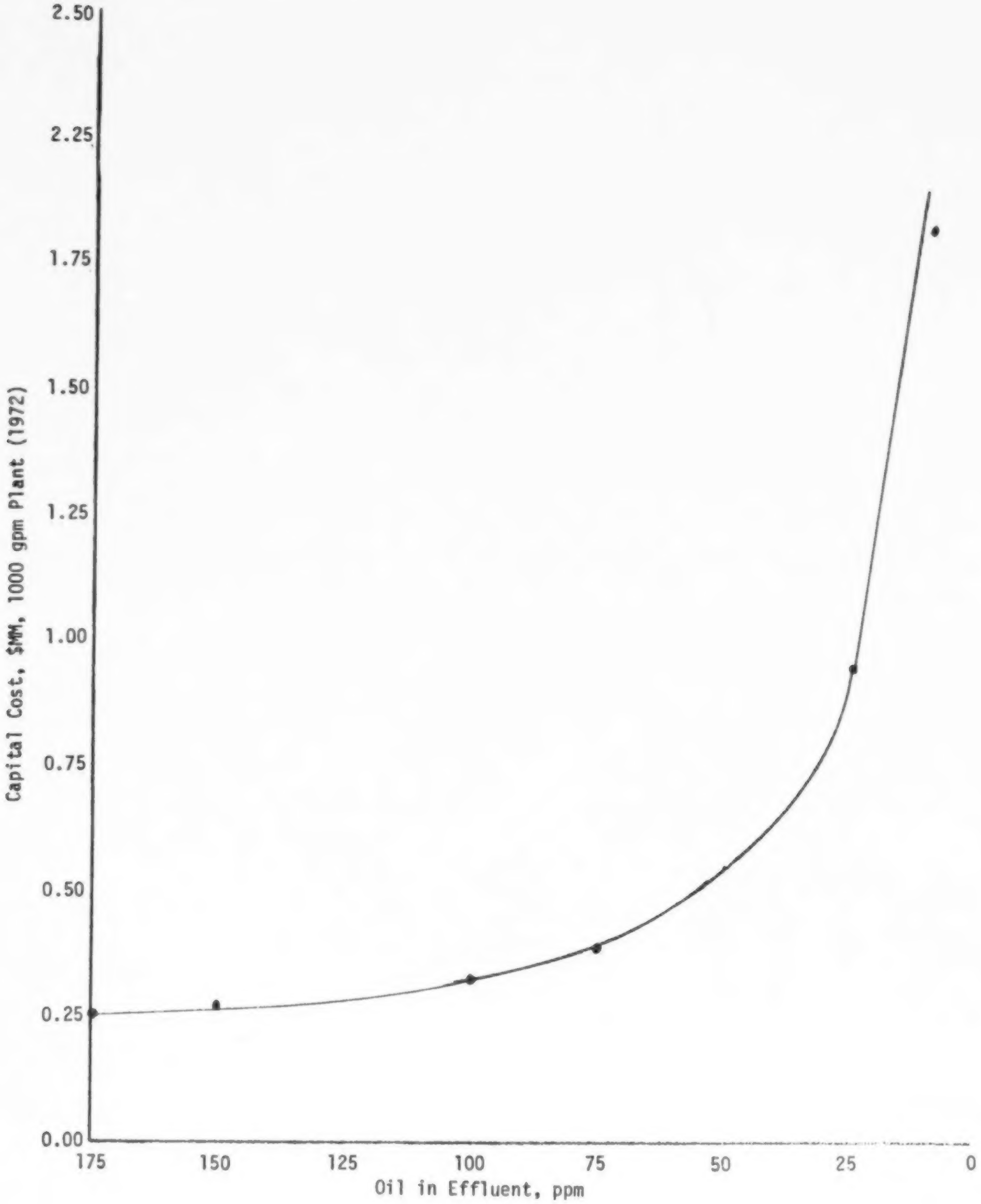

Figure E-4. Capital Cost vs. Quality of Effluent for a 3,780 l/min (1000 gpm) capacity gravity separator is $72,750 annually (includes depreciation of plant at 10%).

6.0 Input Streams

6.1 Raw Wastewater (Stream 1), Figure E-1 - See Table E-1 and E-2.

7.0 Discharge Streams

7.1 Clarified Effluent (Stream 2), Figure E-1 - See Tables E-1 and E-2.

7.2 Recovered Oil (Stream 3), Figure E-1 - No data available.

7.3 Sludge from Settled Solids (Stream 4), Figure E-1 - 3.3% to 59.8% oil (average 22.6%) and 7%-98% oil (average 53%)(71).

8.0 Data Gaps and Limitations

No available data on the use of gravity separation for the treatment of wastewaters from coal conversion facilities. Also, no available data covering feed stream requirements and operating parameters.

9.0 Related Programs

Not known.

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6. Thompson, C.S., et al, Cost and Operating Factors for Treatment of Oily Wastewater, Oil and Gas Journal, November 20, 1972.
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FLOTATION PROCESS

1.0 General Information

1.1 Operating Principle - Separation of solid or liquid particles from a liquid phase by the addition of a gas (usually air and under pressure) to the waste stream (or a fraction thereof) and subsequent release to atmospheric pressure, thereby forming fine bubbles which adhere to and are trapped in the particle structure reducing the gross particle density and hence causing the particles to rise to the surface where they can be removed by skimming. Removal efficiency can be enhanced by the addition of chemical flocculants, particularly when colloidal or emulsified oils are present(1).

1.2 Development Status - Has been used for decades in industrial and municipal wastewater treatment.

1.3 Licensor/Developer - Not a patented or proprietary process; flotation systems/equipment are offered by a large number of water pollution control equipment suppliers.

1.4 Commercial Applications - Dissolved air flotation (DAF) is used by a number of refineries for the removal of oil from wastewaters. In a few refineries dissolved air flotation is used to clarify biologically treated effluents(2). Flotation has also been used for treatment of other industrial wastes (e.g., pulp and paper wastewater) and for sludge thickening. Total flow, split flow and recycle pressurization are the most common DAF systems used in refinery applications(3).

2.0 Process Information (see Figure E-5)

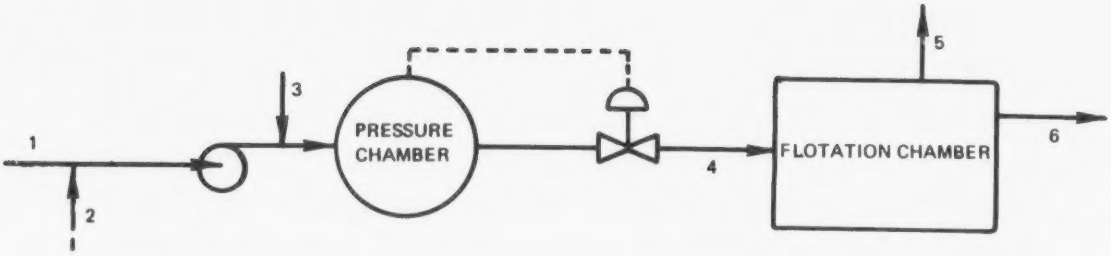
Three most common variations of DAF are total flow, split flow and recycle flow pressurization (depending on whether the entire raw wastewater flow or a portion of the raw wastewater flow or treated effluent is pressurized).

The pressurization is carried out in a pressurized chamber where a short retention is provided for air dissolution. The pressurized liquid is discharged directly to the flotation chamber (total flow pressurization) or mixed with the entire or the remaining portion of the raw wastewater (recycle flow or split-flow pressurization, respectively) and then discharged to the flotation chamber. The solids which float to the surface are skimmed off in the flotation chamber.

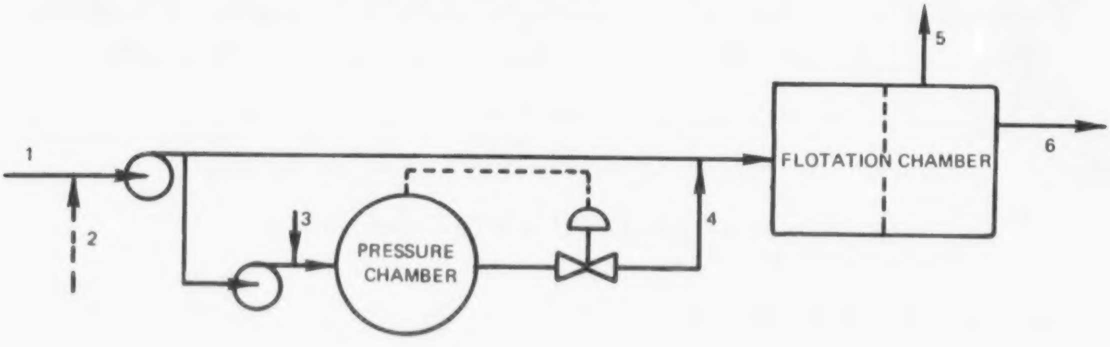
- Desirable features of total flow pressurization include(3):
  - bubbles are released through entire volume of wastewater
  - smaller flotation chamber is required than for recycle pressurization.
- Some desirable features of split flow and recycle pressurization(1,3,5):
  - requires smaller pressurizing pump and reduces pumping cost especially if the DAF system is gravity fed(5)
  - pump control is easier and can be run at a constant rate
  - reduces amount of emulsion that would be formed if all influent was pressurized
  - allows optimum floc formation in portion of feed stream that bypasses pressurization system.

2.1 Equipment

- pressurization pump
- air injection equipment
- pressurization tank
- pressure regulating device
- flotation chamber; rectangular or circular chambers made of concrete, tile or coated steel(3)


1
2
3
PRESSURE CHAMBER
4
5
FLOTATION CHAMBER
6

a. Total Flow Pressurization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PRESSURE CHAMBER
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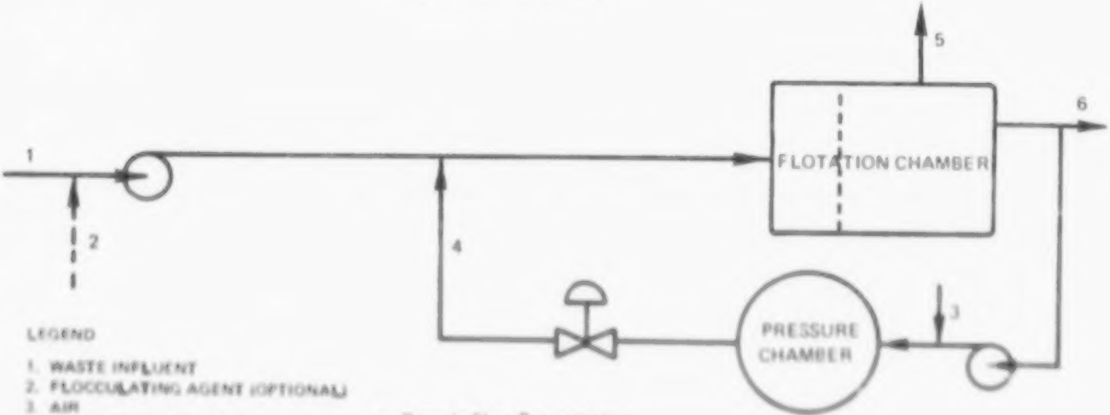
FLOTATION CHAMBER
6

b. Split Flow Pressurization


1
2
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5
FLOTATION CHAMBER
6
3
PRESSURE CHAMBER

LEGEND

1. WASTE INFLUENT
2. FLOCCULATING AGENT (OPTIONAL)
3. AIR
4. PRESSURIZED STREAM
5. OIL SCUM
6. CLARIFIED EFFLUENT

c. Recycle Flow Pressurization

Figure E-5. Dissolved Air Flotation Process

- skimming equipment - flight scrapers or other design
- chemical feeding equipment (if required).

2.2 Feed Stream Requirements - Because of a large number of factors which affect flotation efficiency (e.g., temperature, and nature and concentration of solids), design of flotation systems are usually "tailored" to specific waste application. The design criteria (air-to-solid ratio,* solid rise rate, recycle ratio, etc.) are developed based on laboratory/bench-scale flotation tests. In general, very high concentrations of separable oil (greater than about 1000 ppm) and high wastewater temperature reduce process efficiency(4,5). (Solubility of air in water decreases with the rise in temperature.)

2.3 Operating Parameters

- Stream pressurization
  - total flow system(2,4,6,8) -0.31-0.52 MPa (45-75 psia)
  - partial flow(3) -0.52-0.62 MPa (75-90 psia)
- Retention time
  - pressure retention tank(1,2,3) - 1-5 minutes
  - flotation chamber(1,2,3) - 10-40 minutes
- Flotation chamber overflow rates
  - total flow and split flow(3,4) - 81.4-102 l/min/m^2 (2.0-2.5 gpm/ft^2)
  - recycle flow(4) - 40.7-61 l/min/m^2 (1.0-1.5 gpm/ft^2)
- Air-to-solids ratio - 0.02-0.06

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*Air to solids ratio (A/S) is a dimensionless parameter commonly used for the design of flotation facilities(9): $A/S = [1.3S_a(fP-1)R]/SQ$ where f = saturation factor (less than 1.0); S_a = concentration of air in wastewater at saturation at wastewater temperature, cm^3/l; R = pressurized volume, l; P = absolute pressure, atm; Q = waste flow, l; S = influent suspended solids concentration, mg/l.

2.4 Process Efficiency and Reliability - Depending on wastewater characteristics, unit design/loadings and use of chemical aids, oil, suspended solids and BOD removal ranges of 50% to 100%, 30% to 80%, and 30% to 50% may be expected, respectively(3,4,5). Properly designed and operated flotation units are in operation in many plants; extensive records of trouble-free operation are available for these units.

2.5 Raw Material Requirements

- Air at 0.38 MPa (55 psia) - 0.035 to 0.07 SCM per 1000 (5 to 10 SCF per 1000 gal) of pressurized waste(3).
- Chemical aids(3,4) - Alum, ferric salts, and activated silica are used. Alum and ferric salts are added before or at the pressurization pump. Activated silica is added downstream of the pressure release valve. Amount of chemicals used depends on the type and quantity of the effluent. Common concentrations of alum used in DAF systems are 100-130 mg/l(1).

2.6 Utility Requirements

- Electricity(5) - 0.55 kwh/1000 gal

3.0 Process Advantages

- Handles fluctuations in feed rates well(1,3)
- Captured solids are low in volume compared to large volumes of backwash in filtration(7)
- Effective in reducing BOD and COD(5)
- DAF systems are beneficial in stripping H_2S and NH_3(5)

4.0 Process Limitations

- High temperatures reduce effectiveness(5)
- Does not remove soluble oil(5)
- Does not effectively remove oil emulsions without the use of chemicals(1,3).
- Effectiveness is sometimes unpredictable(3)

5.0 Process Economics

Capital cost for a 3,780 l/min (1000 gal/min) capacity gas flotation system for treatment of oily wastes is $330,000 (1972)(5). Operating cost for the same system is $80,190 annually (1972)(5).

6.0 Input Streams

6.1 Raw Wastewater (Stream 1), Figure E-5 (e.g., oily water from API separator, usually 200-1000 mg/l of free oil(4) - (see Table E-3)

6.2 Air (see Section 2.3)

6.3 Chemical flocculation aids, if required (see Section 2.5)

7.0 Discharge Streams

7.1 Clarified effluent (Stream 6), Figure E-5 (see Table E-3)

7.2 Float (Stream 5), Figure E-5 - Percent solids in the float and characteristics of the float (water content, settleability, etc.) dependent on raw wastewater characteristics and design/operating conditions. For many applications, the solids content of the float is in the 1% to 4% range.

8.0 Data Gaps and Limitations

No data available on the use of flotation for the treatment of wastewaters from coal conversion facilities.

9.0 Related Programs

Not known.

TABLE E-3. DISSOLVED AIR FLOTATION - PERFORMANCE DATA(1)

Influent Oil mg/l	Effluent Oil mg/l	% Removal
1930	128	93
580	68	88
105	26	78
68	15	75
170	52	70*
125	30	71
100	10	90
133	15	89
94	13	86
638	60	91
153	25	83
75	13	82
61	15	75
360	45	87

*No chemical additives used in this case; chemical additives used in all other cases.

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FILTRATION PROCESS

1.0 General Information

1.1 Operating Principle - Wastewater containing suspended solids is passed through a bed of granular material, resulting in deposition of the suspended solids in the bed. When the pressure drop across the bed becomes excessive, the bed is cleaned by backwashing with water. In some cases air scouring of the filter bed is implemented to enhance cleaning(1).

1.2 Development Status - Filtration has been practiced for decades in water treatment plants but only recently has it been used in the treatment of wastewaters(2).

1.3 Licensor/Developer - Not a patented or proprietary process.

1.4 Commercial Applications - Sand filters are employed to polish domestic water supplies and polish industrial wastewaters. Sand filters are currently in use at the Lurgi-type gasification facility at Westfield, Scotland. Hay filters are used in petroleum refining to remove suspended solids (SS) and adsorb oil. Diatomaceous earth filters are used to obtain an extremely high quality effluent. Mixed media filters are used to lengthen the filtering cycle.

2.0 Process Information (see Figure E-6)

Wastewater enters the filtration unit and slowly percolates through the filter media (i.e., sand, charcoal, diatomaceous earth, anthracite, etc.) to the underdrain. As the filtration process proceeds, the pressure drop across the filter (head loss) increases. (At a head loss of 1.5 to 2.4 m of water column or whenever breakthrough occurs, the filtration unit is backwashed to flush the collected SS from the interstices)(1). Backwashing proceeds by flushing water, and in some cases

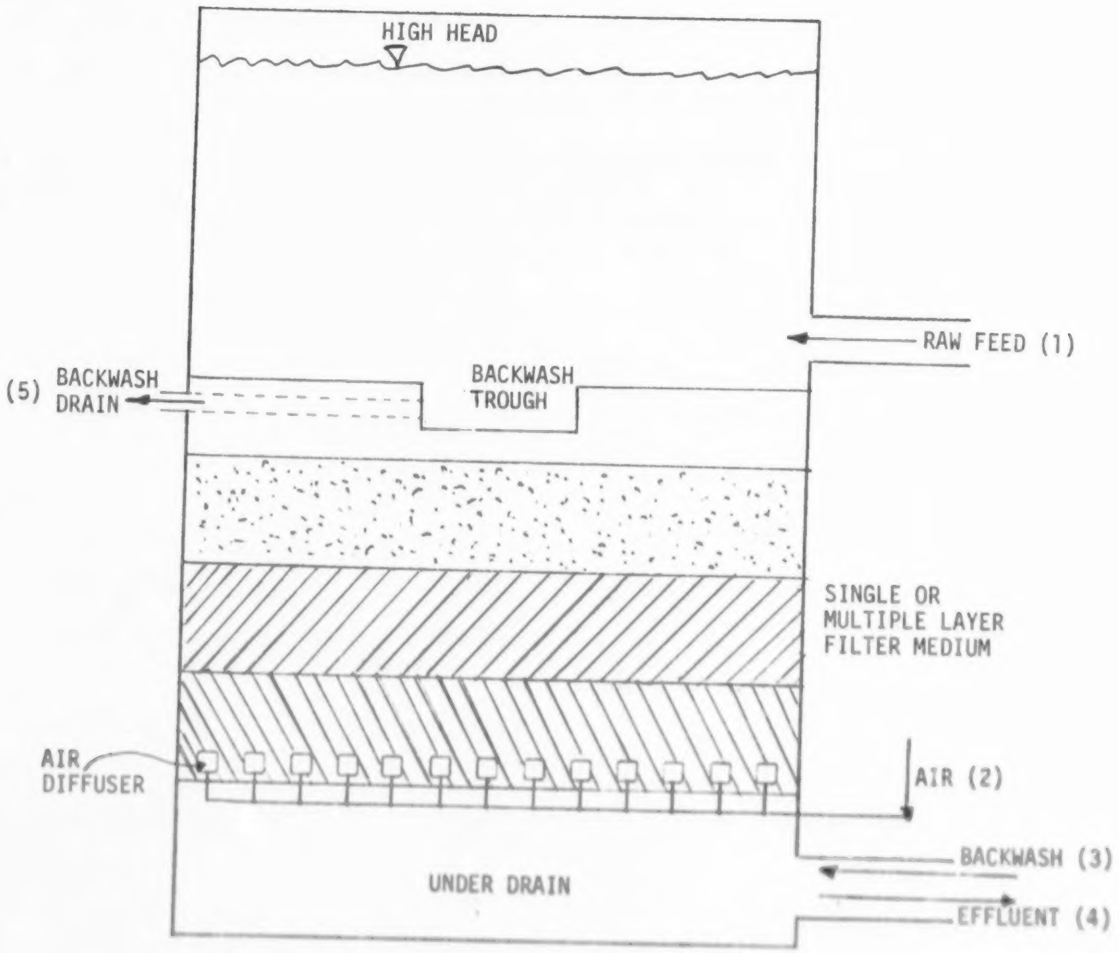
HIGH HEAD
RAW FEED (1)
(5) BACKWASH DRAIN
BACKWASH TROUGH
SINGLE OR MULTIPLE LAYER FILTER MEDIUM
AIR DIFFUSER
AIR (2)
BACKWASH (3)
UNDER DRAIN
EFFLUENT (4)

Figure E-6. Typical Filtration Bed

air, back through the filter bed via the underdrain. Backwash water is collected in the backwash trough and exits the system via the backwash drain.

2.1 Equipment

- Air injection equipment
- Filters media (sand, coal, anthacite, diatomaceous earth, gravel)-60.9 to 71.4 cm (54 to 36 in.)
- Backwash equipment (pump to inject water)
- Piping - cast iron or coal-tar enamel-lined welded steel(4)
- Concrete filter tank although small steel units may be purchased as a whole or assembled in the field

2.2 Feed Stream Requirements

Constituent Present in Influent	Acceptable Concentration(5) in Influent
Solids	100 mg/l
Fiber	10-25 mg/l
Particle size	200 μ
Oil	25-75 mg/l

2.3 Operating Parameters*

	Rate	Operating Time
Backwash	84-1218 lpm/m^2 (2-29 gpm/ft^2)(4,7,9)†	5-15 min.(4,7)
Air scour	0.6-1.5 Nm^3 min/m^2 (2-5 scfm/ft^2)(1,4)	3-10 min.(4)
Waste Influent	168-210 lpm/m^2 (4-5 gpm/ft^2)(4,6)	
Rotating Surface wash	31.5-42 lpm/m^2 (0.75-1.0 gpm/ft^2)(4)	

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*Coal-sand mixed beds.

†Or a rate that will expand the filter bed 20%(7,1).

Begin backwash when breakthrough occurs or when head loss becomes 1.5 to 2.4 m (5 to 8 ft) of water column(4).

2.4 Process Efficiency and Reliability - 60%-95% removal of suspended solids can be expected for granular media filtration(1). Removal efficiencies for other species can be seen in Table E-4 data obtained from operation at the Lake Tahoe reclamation plant. Reliability of filtration is good providing that the system is backwashed at proper intervals before breakthrough occurs(1). Also, oil, fiber and suspended solids can be handled with good reliability as long as their respective influent concentrations are kept within certain limits. Fiber in concentrations greater than 10 to 15 mg/l will cause plugging problems(5). Filters equipped with water backwash can handle 25 mg/l of free oil while filtration equipped with heavy duty air scouring can handle oil in concentrations of 50 to 75 mg/l(5). At higher oil concentrations the oil will cause plugging of underdrains and prevent complete backwashing(5). High concentrations of suspended solids (above 100 mg/l) will cause reduced cycle time(5).

TABLE E-4. TYPICAL REMOVALS BY MIXED-MEDIA FILTERS FROM WASTEWATER PRETREATING BY COAGULATION SEDIMENTATION

Substance	Range (% Removal)
Phosphorus	70 - 95
COD	20 - 45
BOD	40 - 70
Suspended Solids	100
Turbidity	60 - 95

2.5 Raw Material Requirements

- Compressed air - 1.2 Nm^3/m^2 (4 $scfm/ft^2$)
- Backwash water - clarified effluent (permissible to use effluent from another filtration unit) 630-840 lpm/m^2 (15-20 gpm/ft^2) to achieve 38-40% expansion(10)
- Surface wash - 3.45 x 6.89 x 10^5 Pa (50-100 psi) supplied at 31.5 - 42 lpm/m^2 (0.75 - 1.0 gpm/ft^2)
- Polymer aids may be added in doses of less than 0.1 mg/l to enhance filtration

2.6 Utility Requirements - None (except where pumping of influents is required).

3.0 Process Advantages

- High removal efficiencies and reliabilities(1)
- Removes small amounts of suspended solids very well(4)

4.0 Process Disadvantages

- Large volumes of backwash water needed(1)
- Does not handle shock loads well(8)

5.0 Process Economics

For 1000 gpm capacity plant(6) (cost at 1967 dollars)

Capital cost per 1000 liters treated - 0.38¢

Operation and maintenance per 1000 liters treated - 1.4¢

6.0 Input Streams

6.1 Raw Wastewater (Stream 1), Figure E-6 - Wastewater is usually secondary effluent from biologically or chemically clarified waste streams

6.2 Air (Stream 2), Figure E-6 (compressed air)

6.3 Backwash water (Stream 3), Figure E-6 (clarified effluent from other filtration unit)

7.0 Discharge Streams

7.1 Clarified effluent (Stream 4), Figure E-6 - 2-4 mg/l of suspended solids under good conditions(5)

7.2 Backwash effluent (Stream 5), Figure E-6

8.0 Data Gaps and Limitations

No data were found on increased process efficiency when adding polymer aids to filtration. No data available on the quality of backwash streams.

9.0 Related Programs - Not known.

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COAGULATION-FLOCCULATION PROCESS

1.0 General Information

1.1 Operating Principle - Suspended solids and colloidal materials are removed from wastewaters by the addition of chemical coagulants and coagulant aids to produce finely divided precipitates or microflocs. The process of coagulation is followed by flocculation of these small particles into larger clumps or agglomerates which may be removed by sedimentation. Coagulation results from (a) neutralization of negative surface charges on colloidal particles by positively charged metallic or polymeric ions used as coagulants (and/or their hydrolysis products); and (b) the binding and enmeshing actions of the metal hydroxide gels.

1.2 Developmental Status - Commercially available.

1.3 Licensor/Developer - Coagulation-flocculation treatment systems and equipment are offered by numerous suppliers (Ref. 1). Chemical coagulants, coagulant aids and pH adjustment chemicals are available through various chemical supply houses (e.g., Calgon Corporation, Betz, etc.).

1.4 Commercial Applications - An oil flocculation system is in use at the SASOL Lurgi-type coal conversion facility, Sasolburg, So. Africa(2). Numerous applications to treatment of oily wastewaters in petroleum refineries.

2.0 Process Information

2.1 Flow Diagram (see Figure E-7)

- Process Description - Influent wastewaters (Stream 1) are fed to a retention/equalization basin where they are mixed to produce more constant feedwater quantity and quality. The equalized wastewater (Stream 3) is pumped to the coagulation-flocculation unit which usually consists of three chambers: a mixing chamber, a flocculation compartment, and a sedimentation chamber. In the mixing chamber, the wastewater is flash-mixed with chemical flocculants, flocculation aids and pH adjustment chemicals by means of vertical or horizontal mechanical paddles. The wastewater passes from the mixing chamber to the flocculation compartment where it is agitated by slowly moving paddles, then flows into the sedimentation chamber by means of an inlet device which distributes the waste uniformly throughout the cross-sectional area of the chamber. Clarified waters (Stream 4) leave the sedimentation chamber over a weir. Residual sludge (Stream 5) is scraped from the bottom of the sedimentation chamber and discharged.

2.2 Equipment(3)

- Coagulation-flocculation unit - Two basic types: (a) the sludge-blanket unit which combines mixing, flocculation and settling in a single unit; and (b) the conventional system using a rapid mix tank, followed by a flocculation tank containing longitudinal paddles which provide slow mixing; and a conventional settling tank.

- Retention/equalization basin

- Pumps

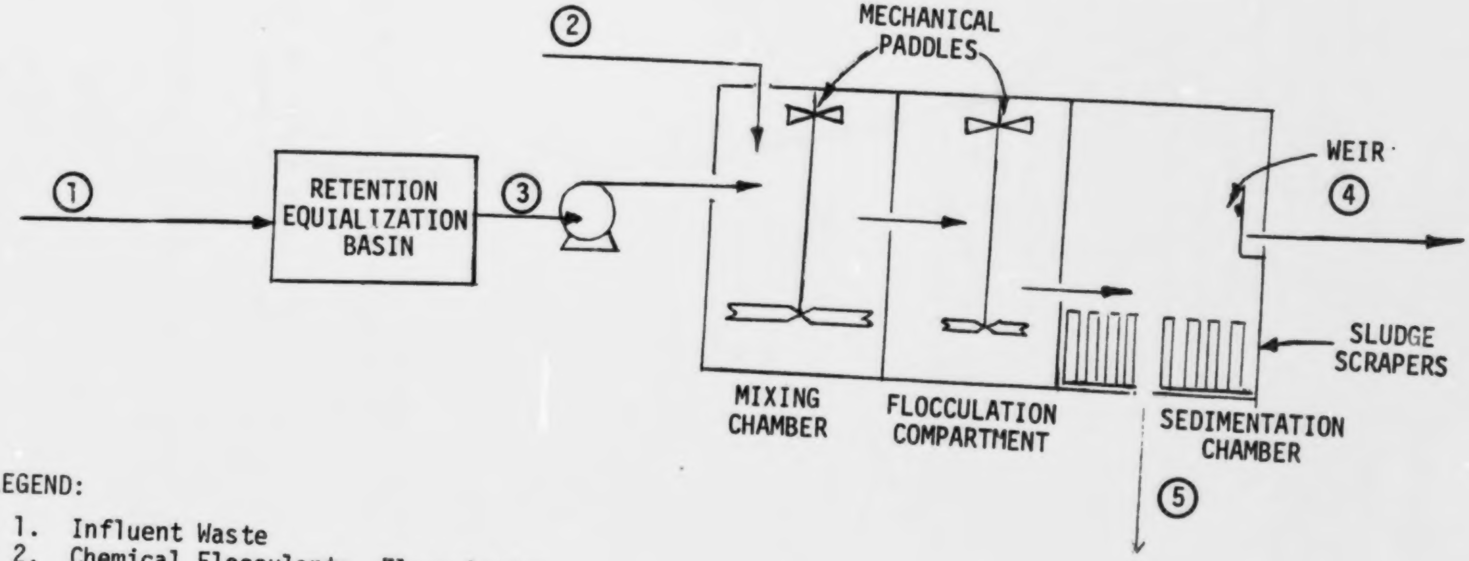
- Mechanical paddles

2.3 Feed Stream Requirements(3,4)

- Flow rate - For ease of operation and constant effluent quality, the influent rate to the coagulation-flocculation unit should be as uniform as possible.

- Composition - Composition of the influent waste should be as uniform as possible to minimize the number of adjustments of chemical dosages required.

- pH - Optimum pH for coagulation, as determined by laboratory tests, should be maintained.


①
RETENTION EQUIALIZATION BASIN
③
②
MECHANICAL PADDLES
MIXING CHAMBER
FLOCCULATION COMPARTMENT
SEDIMENTATION CHAMBER
WEIR
④
SLUDGE SCRAPERS
⑤

LEGEND:

1. Influent Waste
2. Chemical Flocculants, Flocculation Aids, and pH Adjusters
3. Equalized Wastewaters
4. Clarified Effluent
5. Flocculated Sludge to Treatment/ Disposal

Figure E-7. Schematic of "Sludge Blanket" Coagulation - Flocculation System

2.4 Operating Parameters(4,5) - Coagulation, flocculation and settling times vary with the specific waste being treated; optimum conditions can be determined by lab-scale testing of the wastewaters (e.g., "jar tests"). The period for flash mixing of coagulation chemicals into the waste usually varies from 30 seconds to 5 minutes while flocculation times range 5-30 minutes. Retention time in the sedimentation chamber varies from 2 to several hours. Requirements are determined by sedimentation tests of the flocculated water. See Table E-5.

2.5 Process Efficiency and Reliability - Efficiency depends upon the design of the system, coagulant dosage, temperature and on the characteristics of the wastewaters. The chemical nature of the wastewater contaminants (e.g., suspended solids, colloidal materials, etc.) determines their propensity for coagulation. Hydrophobic contaminants (e.g., clays, inert solids) have no adsorption affinity for aqueous media, and are readily susceptible to coagulation. Hydrophilic contaminants (e.g., emulsified oils) tend to adsorb or absorb water which retards coagulation and flocculation, and special coagulant aids are often required to achieve effective coagulation. Coagulation-flocculation processes have been widely used and proven reliable for treatment of a range of industrial and municipal wastewaters (e.g., paperboard, laundromat, chemical, synthetic rubber, and vegetable processing wastes). See Table E-6.

2.6 Raw Materials Requirements

- Coagulation chemicals - Commercial grade alum $[Al_2(SO_4)_3 \cdot 14H_2O]$, ferric salts, high molecular weight polyelectrolytes, etc. See Table E-7.
- Coagulation aids - Activated silica, inorganic salts (e.g., $CaCl_2$), etc. See Table E-7.
- pH adjustment - Sulfuric acid, sodium hydroxide, lime. See Table E-7.

2.7 Utility Requirements

- Electricity - Used for driving pumps, mechanical paddles. Requirements vary with the specific design and removal efficiency desired.

TABLE E-5. COMPARISON OF LIME, ALUM AND FERRIC CHLORIDE TREATMENT*(7)

Parameter	$Ca(OH)_2$	Alum†	$FeCl_3$‡
Chemical Cost, ¢/kg (¢/lb)	2.48 (1.25)	7.7 (3.5)	9.9 (4.5)
Chemical Dosage, mg/l	350	150	100
Polymer, mg/l @ $2.75/kg	--	0.5	0.5
Acid Dosage, mg/l H_2SO_4 @ 2.2¢/kg (1¢/lb)	200	--	--
Total Chemical Cost, ¢/1000 liter (¢/1000 gal)	1.4 (5.3)	1.3 (4.9)	1.2 (4.7)
Operating pH	10.2-10.8	6.5-7.5	6.5-7.5
Rise Rate, pm/m^2 (gpm/ft^2)	30.5 (0.75)	20.32 (0.50)	20.32 (0.50)
Thickened Sludge, %	10-15	3-5	3-5
Thickener Loading, kg/day-m^2 (lb/day-ft^2)	10.2-15.3 (50-75)	1.0-2.0 (5-10)	1.0-2.0 (5-10)
Vacuum Filtration Rate, kg/hr/m^2 (lb/hr/ft^2)	1.6-2.0 (8-10)	0.4-0.6 (2-3)§	0.4-0.6 (2-3)§

*Data and calculations shown are based partially on results obtained from a (25 gpm) pilot plant using South Salt Lake Sewage conducted by Sanitary Engineering R&D Dept. of Eimco Corp.

†Filter alum - $Al_2(SO_4)_3 \cdot 14H_2O$

‡40 Percent liquid solution by weight

§Sludge conditioning chemical required

TABLE E-6. EFFICIENCY OF COAGULATION-FLOCCULATION TREATMENT OF INDUSTRIAL AND MUNICIPAL WASTEWATERS(3)

	Waste Type					
	Paperboard	Ball-bearing	Laundromat	Latex Paint	Synthetic Rubber	Vegetable Processing
Coagulation Agents Added						
Alum	50 mg/1	800 mg/1	--	345 mg/1	100 mg/1	--
Silica	5 mg/1	--	--	--	--	--
H_2SO_4	--	450 mg/1	--	--	--	--
Polyelectrolyte	--	45 mg/1	--	--	--	--
Cationic Surfactant	--	--	88 mg/1	--	--	--
Calcium Chloride	--	--	480 mg/1	--	--	--
Lime (1b/1b BOD)	--	--	--	--	--	0.5
Constituent Removal (%)						
BOD	--	--	54.7	91.6	82.3	35-70
SS	95.7-86.6	92.6	--	--	--	--
Oil and Grease	--	90.7	--	--	--	--
Fe	--	91.1	--	--	--	--
$PO_4^=$	--	95.9	43.8	--	--	--
COD	--	--	66.6	95.8	82.4	--
TSS	--	--	--	82.5	--	--
pH	--	10.3 (influent) 7.1 (effluent)	7.1 (influent) 7.7 (effluent)	3.5-4.0 (influent)	6.7 (influent)	
Detention Time, hr	1.7	--	--		--	--
Sludge, % Solids	2-4	--	--	3	--	--

TABLE E-7. CHEMICAL COMPOUNDS USED IN COAGULATION-FLOCCULATION PROCESSES(4)

Compound	Formula	Commercial Strength	Grades Available	Weight, kg/m^3 (Pounds per Cubic Foot)	Suitable Handling Materials	Remarks
Coagulants						
Aluminum sulfate	$Al_2(SO_4)_3 \cdot 14H_2O$	17 percent Al_2O_3	Lump Powder Granules	Powder: 613-718 (38-45) Other: 909-1069 (57-67)	Lead Rubber Silicon Iron	Coagulation and sedimentation systems; prior to pressure, filters for removal of suspended matter and oil
Sodium aluminate	$Na_2Al_2O_4$	55 percent Al_2O_3	Crystals	797-957 (50-60)	Iron Steel Rubber Plastics	Usually added with soda ash to softeners
Ammonium alum	$Al_2(SO_4)_3(NH_4)_2SO_4 \cdot 24H_2O$	11 percent Al_2O_3	Lump Powder	957-1085 (60-68)	Lead Rubber Silicon Iron Stoneware	Coagulation systems - not widely used
Potash alum	$Al_2(SO_4)_3 \cdot K_2SO_4 \cdot 24H_2O$	11 percent Al_2O_3	Lump Powder	1021-1085 (46-68)	--	Coagulation systems - not widely used
Copperas	$FeSO_4 \cdot 7H_2O$	55 percent $FeSO_4$	Crystals Granules	1005-1053 (63-66)	Lead Tin Wood	Suitable coagulant only in pH range of 8.5 to 11.0
Chlorinated copperas	$FeSO_4 \cdot 7H_2O + 1/2Cl_2$	48 percent $FeSO_4$	--	--	--	Ferrous sulfate and chlorine are fed separately
Ferric sulfate	$Fe_2(SO_4)_3$	90 percent $Fe_2(SO)_3$	Powder Granules	957-1116 (60-70)	Lead Rubber Stainless steel Plastics	Coagulation - effective over wide range of pH, 4.0 to 11.0
Ferric chloride hydrate	$FeCl_3 \cdot 6H_2O$	60 percent $FeCl_3$	Crystals	--	Rubber Glassware Stoneware	Coagulation - effective over wide range of pH, 5.0 to 11.0
Magnesium oxide	MgO	95 percent MgO	Powder	399-588 (25-35)	Iron Steel	Essentially insoluble - fed in slurry form

(continued)

TABLE E-7. Continued

Coagulant Aids*						
Bentonite	--	--	Powder	967 (60)	Iron Steel	Essentially insoluble - fed in slurry form
Sodium silicate	$Na_2O(SiO_2)_{3-25}$	40 Be solution	Solution	1372 (86)	Iron Steel Rubber	--
pH Adjusters						
Lime, hydrates	$Ca(OH)_2$	90 percent $Ca(OH)_2$	Powder	393-797 (25-50)	--	pH adjustment and softening
Soda ash	Na_2CO_3	99 percent Na_2CO_3	Powder	542-829 (34-52)	--	pH adjustment and softening
Caustic soda	NaOH	98 percent NaOH	Flake Solid Ground Solution		--	pH adjustment, softening, oil removal systems
Sulfuric acid	H_2SO_4	100 percent H_2SO_4	Liquid	--	--	pH adjustment

*Other compounds, for which no information is available, suitable as coagulant aids are activated silica, clay, activated carbon causticized starches, and ethyl cellulose.

3.0 Process Advantages(4,5)

- Effective for removal of suspended solids and oils from a variety of wastewaters, including nonbiodegradable and refractory organics.
- Minimum utility and raw materials requirements.
- Minimum maintenance requirements for most systems.
- Relatively inexpensive method for removal of oil and suspended solids.

4.0 Process Limitations(4,5)

- Process is highly sensitive to fluctuations in wastewater characteristics; wastewater composition must be as uniform as possible.
- Unreacted coagulant chemicals may cause after-flocculation when the clarified effluent is discharged into receiving waters.
- Large quantities of sludge are generated which may require dewatering by filtration or centrifugation and disposal, either by incineration or landfill.
- Iron and aluminum salts form gelatinous hydroxide flocs that are difficult to dewater in many cases.
- Use of iron and aluminum salts add large amounts of ions (chlorides or sulfates) to the wastewater.
- Polyelectrolytes used alone are ineffective for removal of phosphorous.

5.0 Process Economics

Capital and operating equipment costs depend on the type and size of the coagulation-flocculation unit used. Chemical costs depend on the specific chemical(s) utilized and on the quantity of wastewater to be treated. The prices of common coagulation chemicals (1978 dollars) are: \$142/tonne (\$129/ton) of alum; \$27.60/tonne (\$25/ton) of lime; \$2977-5513/tonne (\$2700-5000/ton) of polyelectrolytes(6). See Table E-6.

6.0 Input Streams

6.1 Influent Waste (Stream 1) - Wastewater characteristics will vary, depending on the source. See Table E-6 for typical industrial/municipal wastewater characteristics.

6.2 Chemical Flocculants, Flocculation Aids, and pH Adjusters (Stream 2) - See Section 2.6.

7.0 Intermediate Streams

7.1 Equalized Wastewater (Stream 3) - Composition will vary, depending on that of the influent wastes (Stream 1).

8.0 Discharge Streams

8.1 Clarified Effluent (Stream 4) - See Table E-6. Effluent characteristics will vary, depending on the composition of the influent waste. Effluent will also contain unreacted, excess coagulation chemicals.

8.2 Sludge (Stream 5) - See Table E-6. Will contain flocculated oil, suspended solids and colloidal matter.

9.0 Data Gaps and Limitations

Effective use of coagulation-flocculation processes on oily and colloidal wastewaters from coal gasification operations will depend on trial-and-error experimentation to determine the most suitable processes and conditions, since actual operating conditions for these waters are unknown.

10.0 Related Programs - None known.

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Dissolved Gases Removal Module

Steam Stripping
USS Phosam W
Chevron WWT

STEAM STRIPPING PROCESS

1.0 General Information

1.1 Operating Principle - Removal of hydrogen sulfide and/or ammonia from sour waters by stripping with steam (the most common stripping medium*), flue gas or an inert gas. The stripping efficiency can be enhanced by adjustment of the pH of the sour water. Depending on the system design and operating conditions, other volatile components such as phenols and cyanides may also be partially removed during stripping.

1.2 Development Status - Process has been used commercially for several decades, primarily in petroleum refineries.

1.3 Licensor/Developer - Not a patented or proprietary process.

1.4 Commercial Applications - Widely employed in refineries for removal of H_2S and NH_3 from sour waters. The Lurgi facility at SASOL, S.A. employs steam stripping for wastewater treatment and ammonia recovery$^{(11)}$.

2.0 Process Information

2.1 Flow Diagram (see Figure E-8) - Sour water is fed to the top of the stripping tower and flows downward countercurrent to steam over trays or packing. Overhead vapors may be cooled to condense moisture (in a reflex drum) if the offgas is to be treated for sulfur

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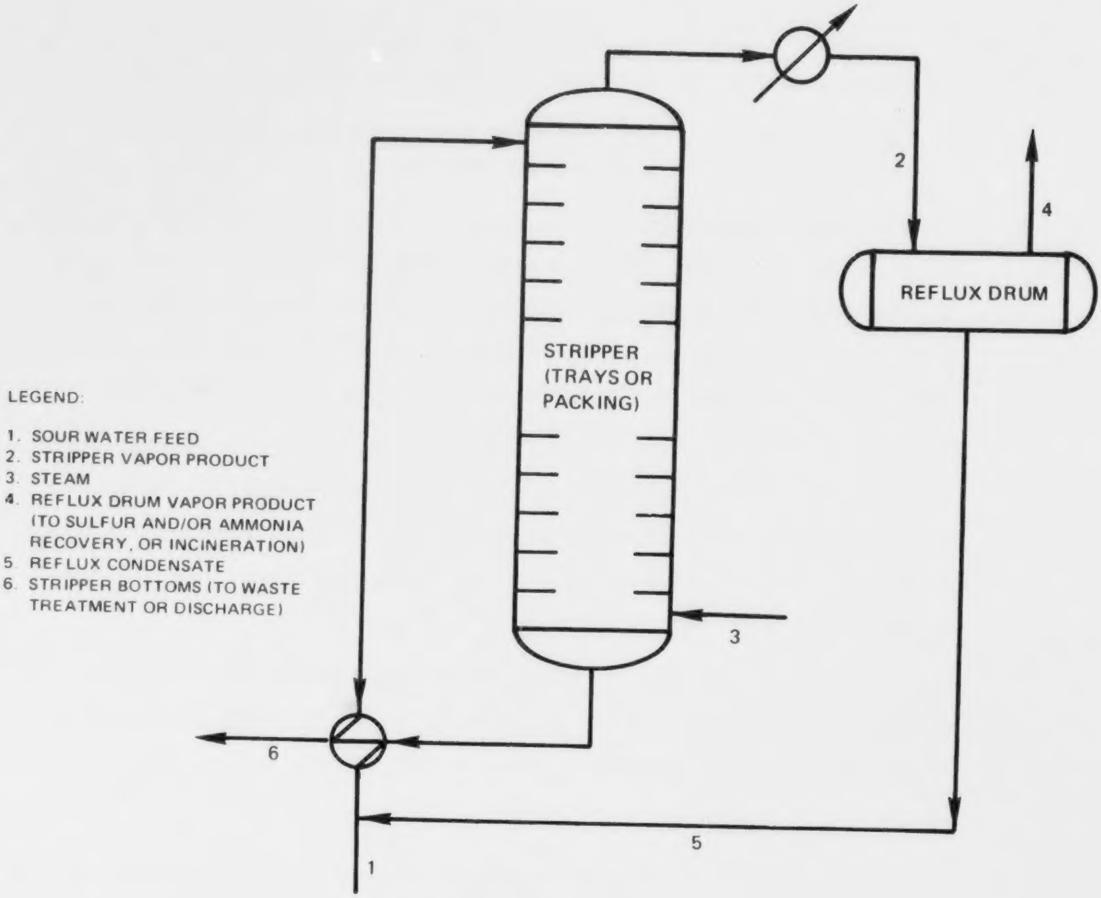
*Based on a recent survey of refineries conducted by the American Petroleum Institute (API)(1), the vast majority of sour water strippers use steam as the stripping medium. Use of flue gas, though suitable for H_2S removal, yields poor ammonia removal efficiencies. Only steam stripping is covered in this data sheet. Licensed processes (Chevron WWT and PHOSAM W) which feature both stripping and ammonia and sulfur recovery are covered by separate data sheets.


2
4
REFLUX DRUM
STRIPPER (TRAYS OR PACKING)
3
6
5
1

LEGEND:

1. SOUR WATER FEED
2. STRIPPER VAPOR PRODUCT
3. STEAM
4. REFLUX DRUM VAPOR PRODUCT (TO SULFUR AND/OR AMMONIA RECOVERY, OR INCINERATION)
5. REFLUX CONDENSATE
6. STRIPPER BOTTOMS (TO WASTE TREATMENT OR DISCHARGE)

Figure E-8. Refluxed Sour Water Stripper and/or ammonia recovery. Reflux is not employed when the offgas is incinerated. Stripper bottoms are commonly cooled by heat exchange with feed water.

2.2 Equipment(1)

- Stripping Tower - Carbon steel shell and lining. Tower may contain packing (ceramic) or trays (carbon steel). All towers constructed since 1970 employ trays according to an API survey.
- Reflux Drum - Linings commonly carbon steel, although stainless sometimes used to minimize corrosion.

2.3 Feed Stream Requirements - Hydrocarbons in feed can cause fouling of stripper unit and reflux system, and can create further downstream problems if stripper offgas is fed to a sulfur recovery plant. A surge vessel with skimming facilities and depressurization equipment is commonly employed ahead of the sour water stripper to minimize organics in stripper feed(2).

Carbonates in sour feed can lead to tower deposits and can limit hydrogen sulfide removal efficiency. High carbonate wastewaters are either neutralized prior to stripping or handled by means other than stripping(4).

Temperature of feed affects steam consumption in the tower. A temperature of about 393°K (250°F) is an ideal feed temperature, with about 338°K (150°F) being a practical minimum(3).

2.4 Operating Parameters

- Temperature(3): 355°K (180°F) is approximate minimum operating temperature for reflux drum overhead to inhibit ammonium hydrosulfide deposition.
- Tower Bottom Pressure(3,6): 170-400 kPa (17-40 psia)
- Loading: Depends upon efficiency desired, liquid flow rate, steam/sour water ratio, and nature of packing or trays used (see Section 2.6 for steam quantities used).

2.5 Process Efficiency and Reliability - With efficient steam stripping about 99+% H_2S removal, 90%-95% NH_3 removal, and 50-70% phenol removal may be realized(4). Sour water stripping units commonly show good reliability, although problems with foaming and fouling can occur when organics are present in the feed or temperature is too low in the reflux drum (allowing ammonium hydrosulfide to precipitate).

2.6 Raw Material Requirements

- Steam: 0.036 - 0.32 kg/l (0.3 - 2.7 lbs/gal) depending on tower packing and degree of ammonia removal required(1). A typical refinery steam rate is about 0.13 kg/l (1.0 lb/gal) feed. A design case for stripping of sour waters from a coal gasification operation specified 0.18 l/kg (1.5 lbs/gal)(0.9).
- Caustic or Acid(2): Lime or sodium hydroxide may be added to release feed ammonia from relatively acidic sour waters. Similarly, flue gas, hydrochloric or sulfuric acid may be added to alkaline sour waters to enhance hydrogen sulfide removal. Quantities needed depend on the buffer capacity of the sour water feed(10).

2.7 Utility Requirements

- Steam (see Section 2.6)
- Electricity(9): about 0.92 kwh /1000 l (3.5 kwh /1000 gal feed)
- Cooling water(9): about 0.6 l/l feed

3.0 Process Advantages

- High degree of removal of hydrogen sulfide from sour waters.
- Ammonia levels in stripper water are relatively independent of feed concentration.
- Process is widely used and reliable.
- Equipment can be constructed primarily of carbon steel.
- Low utility requirements.
- Relatively inexpensive operation.
- Vapor product can be processed for ammonia and/or sulfur recovery.

4.0 Process Limitations

- Hydrogen sulfide and ammonia removal efficiencies depend upon the buffer capacity of the sour feed.
- Overhead vapors from stripper are corrosive and can lead to the formation of deposits (primarily NH_4HS).

- Organics can cause tower fouling, can affect ammonia and hydrogen sulfide removal efficiencies, and can carry over to vapor product.
- Stripper bottoms generally require additional control before discharge.

5.0 Process Economics

Capital cost for a 4 x 10^6 l/day (1 MGD) capacity sour water stripping operation for a coal gasification facility is estimated at about 1 million dollars (1976)(5). Operating costs depend largely on steam rate and energy source for its generation. The operating cost for the above sour water treatment plant is estimated at about $240,000 in 1975 dollars.

6.0 Input Streams

6.1 Sour Water Feed (Stream 1) - Ammonia levels in refinery sour waters are commonly in the range of 1000-10,000 mg/l (see Table E-8 for the range of feed ammonia levels encountered in an API survey(1)). Hydrogen sulfide levels range from 300 to 10,000 mg/l(4,8); phenol levels range from 30 to 800 mg/l(4). Table E-8 presents data on the sources and composition of sour waters in an example petroleum refinery(2). Gas liquor feed at the SASOL Lurgi gasification plant contains 1.0 to 1.2 weight % ammonia.

6.2 Steam (Stream 3) - see Section 2.6 and Table E-9

TABLE E-8. SOURCES AND COMPOSITION OF SOUR WATERS IN AN EXAMPLE PETROLEUM REFINERY(2) - STREAM 1

Stream Source	Typical Flow Rate l/min (gpm)	Ammonia Concentration (mg/l)	Sulfide Concentration (mg/l)
Fluid Catalytic Cracker	570 (150)	3,800	11,125
Gas Plant/Sour Crude Unit	95 (23)	1,400	1,706
HDS* Unit Foul Water	175 (46)	300	471
Sulfur Plant Sour Water	217 (57)	280	770
Miscellaneous	95 (25)	1,000	4,950
Total (or average)	1,380 (363)	1,850	5,350

***Hydrodesulfurization**

TABLE E-9. PERFORMANCE DATA FOR REFINERY SOUR WATER STRIPPERS WITH HIGH AMMONIA REMOVAL(1) - STREAMS 1, 3 AND 6

Tower Media	Average Steam Rate kg/l (lbs/gal)	Average Ammonia in Feed (mg/l)	Average Ammonia in Bottoms (mg/l)	Minimum Ammonia in Bottoms (mg/l)
		Refluxed Strippers		
10 valve trays	1.4 (3.1)	2500	78	25
8 valve trays	1.0 (2.2)	1200	25	--
30 sieve trays	1.1 (2.4)	1720	68	--
30 sieve trays	2.5 (5.5)	430	64	--
24 sieve trays	0.6 (1.3)	74	63	--
23 sieve trays	1.6 (3.5)	4000	100	40
52 valve trays	--	1600	65	--
5 glitch trays	7.8 (17.2)	5410	45	19
20'-3" Raschig rings	1.3 (2.9)	3550	--	37
10 flex trays	1.8 (4.0)	2000	200	25
15'-3" Raschig rings	1.5 (3.3)	1400	80	7
18 trays	--	19,000	80	--
20 bubble cap trays	--	2000	15	10
12 Socony trays	1.2 (2.6)	32,200	56	--
20 sieve trays	--	1600	25	7
		Non-Refluxed Strippers		
8 bubble cap trays	1.5 (3.3)	960	50	30
6 shower trays	0.3 (0.7)	1850	96	--
15'-3" Raschig rings	0.6 (1.3)	1200	65	36
15'-3" saddles	0.2 (0.4)	2600	200	34
8 valve trays	1.9 (4.2)	5450	56	--
28 bubble cap trays	0.8 (1.8)	2625	10	--
5 valve trays	0.4 (0.9)	215	76	--
8 flex trays	2.7 (5.9)	4400	11	10

7.0 Intermediate Streams

7.1 Stripper Vapor Product (Stream 2) - no data available (this stream may be a discharge stream in the case of a non-refluxed stripper).

7.2 Reflux Condensate (Stream 5) - see Table E-10 (applies only to refluxed strippers).

8.0 Discharge Streams

8.1 Stripper Bottoms (Stream 6) - see Table E-11 and Table E-9.

8.2 Reflux Drum Vapor Product (Stream 4) - Limited data available; H_2S, NH_3, and CO_2 will be present in offgas in approximately the same ratio as found in feed water (assuming near equal removal efficiencies). The offgas may contain other volatile organics (e.g., phenols, light hydrocarbons) and inorganics (e.g., HCN). At the SASOL Lurgi gasification facility, ammonia stripper column overhead contains 6% ammonia and 0.1% H_2S.

TABLE E-10. COMPOSITION OF SOUR WATER STRIPPER REFLUX CONDENSATE AT A LARGE REFINERY*(1) - STREAM 5

Steam Rate† - kg/l (lbs/gal)	Reflux Ammonia (mg/l)	Reflux H_2S (mg/l)
1.20	32,600	16,300
1.41	36,300	30,600
1.58	42,600	28,600
1.76	26,300	17,700
1.90	30,300	8,600
2.23	10,000	9,200
2.87	52,300	12,500

*10 actual stages (or trays) in tower.

†Steam rate is only one variable influencing reflux ammonia and hydrogen sulfide levels; data reflect varying operating conditions.

TABLE E-11. CHARACTERISTICS OF REFINERY SOUR WATER STRIPPER BOTTOMS(7)* - STREAM 6

Example Refinery No.	1	2	3	4	5	6
NH_3 (as N)	28	30	30	12	50	50
Sulfide (as H_2S)	0.01	0.1	0.1	0.1	0	0.6
Phenols	110	33	80	50	--	--
BOD	--	--	288	121	--	--
COD	--	--	387	203	--	--
TOC	--	--	119	32	--	--
TSS	28	--	--	6	--	--
Total alkalinity**	88	140	68	100	46	94
Chloroform extractables	13	--	71	--	--	--
Ca^{++}	5	0.3	13	2	2	1
Mg^{++}	0.5	0.1	14	0	0	0
SiO_2	< 2	1.3	4.4	--	--	--
Cl^-	39	1.5	260	28	142	93
$SO_4^=$	16	37	125	--	32	34
Total $PO_4^{\equiv}$	3	0.4	2	--	--	--
NO_2^-	0	253	276	--	--	--
NO_3^-	<1	<1	< 1	--	--	--
Cu^{++}	0.05	0.02	0.12	--	0.1	--
Fe^{+2} & $^{+3}$	1.6	0.6	0.5	--	9.4	--
Zn^{++}	0.0	0.0	0.0	--	0.0	--
Specific conductance	250	500	1200	280	--	425
pH	6.8	7.7	8.7	9.6	6.8	9.1

*mg/l except pH and specific conductance (μmhos @ 18°C)
**mg/l $CaCO_3$

9.0 Data Gaps and Limitations

Data gaps and limitations relate primarily to the performance of sour water strippers with regard to minor constituents such as oils, phenolics, amines, and cyanides. No data for actual applications to coal gasification are known.

10.0 Related Programs

No programs are known to be underway or planned which are aimed at the assessment of sour water stripper performance in coal gasification applications.

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USS PHOSAM W PROCESS*

1.0 General Information

1.1 Operating Principles - Ammonia is absorbed from a gas stream (usually overhead vapors from a sour water stripper) by countercurrent flow of an ammonium phosphate solution. The ammonia-enriched solution is subsequently steam stripped at elevated pressure to release the absorbed ammonia. The resulting water/ammonia vapor stream is fractionated to produce anhydrous ammonia. The absorption/regeneration reaction may be represented as follows:

$$(NH_4)_{1.3}H_{1.7}PO_4 + 1/2\ NH_3 \rightleftharpoons (NH_4)_{1.8}H_{1.2}PO_4$$

1.2 Development Status - commercial; several PHOSAM units are currently in operation on coke oven gases.

1.3 Licensor - USS Engineers and Consultants, Inc. (UEC)
600 Grant Street
Pittsburg, PA 15230

1.4 Commercial Applications(2) - The PHOSAM process is used at the U.S. Steel's Clairton coke facility (Pittsburg, PA) and nine other PHOSAM plants are operating worldwide; others are in the design and construction phase. PHOSAM W is licensed to at least one proposed coal gasification plant.

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*The PHOSAM Process is for application to byproduct coke production. The PHOSAM W refers to the application of the process to other wastewaters and gases.

2.0 Process Information

2.1 Flow Diagram (see Figure E-9 for one design of the PHOSAM W process for treating sour water)* - Sour water enters a steam stripper where free NH_3, H_2S, CO_2 and other acid gases and volatile organics are stripped. The top of the stripper is an ammonia absorber where lean ammonium phosphate solution contacts the sour vapors and absorbs ammonia and small amount of acid gases. Stripped sour water leaves the bottom of the stripper. Rich ammonium phosphate solution is purged of acid gases in a contactor and sent to a high pressure steam stripper for ammonia removal. Lean solution returns to the absorber, while the ammonia is separated from water by distillation. Caustic is added to the fractionation system to inhibit acid gas accumulation in the still. Still bottoms are returned to the sour water stripper. Reboilers may be used on the columns, if condensate recovery is required.

2.2 Equipment(3) - Based on a design for 13.7 x 10^6 l/day (3.6 MGD) sour water treatment.

- "Superstill" consisting of a sour water stripper and absorber

	Height	Diameter
Bottom	25 m (84 ft)	4.4 m (14.5 ft)
Top	18 m (61 ft)	2.9 m (9.5 ft)

- PHOSAM Stripper

  Height - 21 m (70 ft)

  Diameter - 2.9 m (9.5 ft)

- Fractionator

  Height - 20 m (65 ft)

  Diameter - 1.6 m (5.25 ft)

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*Process can also be designed to handle ammonia-containing gas streams, in which case the sour water stripper is omitted.

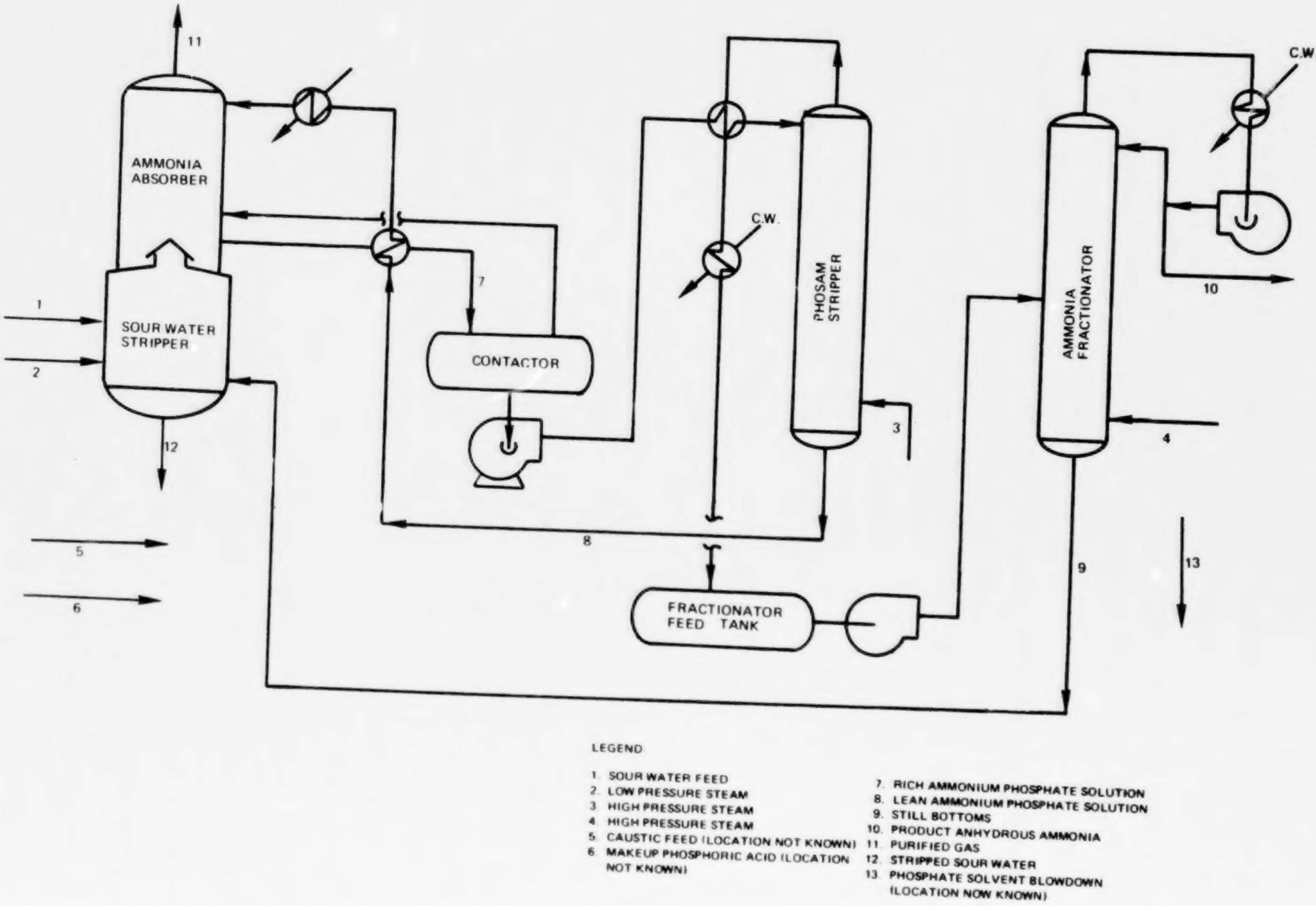
11
AMMONIA ABSORBER
SOUR WATER STRIPPER
1
2
12
5
6
7
CONTACTOR
8
C.W.
PHOSAM STRIPPER
3
FRACTIONATOR FEED TANK
C.W.
AMMONIA FRACTIONATOR
10
4
9
13
LEGEND
1. SOUR WATER FEED
2. LOW PRESSURE STEAM
3. HIGH PRESSURE STEAM
4. HIGH PRESSURE STEAM
5. CAUSTIC FEED (LOCATION NOT KNOWN)
6. MAKEUP PHOSPHORIC ACID (LOCATION NOT KNOWN)
7. RICH AMMONIUM PHOSPHATE SOLUTION
8. LEAN AMMONIUM PHOSPHATE SOLUTION
9. STILL BOTTOMS
10. PRODUCT ANHYDROUS AMMONIA
11. PURIFIED GAS
12. STRIPPED SOUR WATER
13. PHOSPHATE SOLVENT BLOWDOWN (LOCATION NOW KNOWN)

Figure E-9. USS PHOSAM W Process(1)

- Heat Exchangers - approximately 5640 m^2 (60,000 ft^2) of surface area

PHOSAM W absorber, strippers and fractionator are stainless steel clad. Sour water stripper is carbon steel.

2.3 Feed Stream Requirements - Tars and pitches can cause fouling problems in sour water stripper reboiler or bottoms interchangers if used.

Temperature of feed affects steam consumption in the sour water stripper and heat exchanger surface requirements(2). Feed at its bubble point is ideal, but any temperature is acceptable.

2.4 Operating Parameters

Temperature(2):	Absorber - 378°K (220°F) PHOSAM stripper - 465°K-475°K (380°F-400°F)
Pressure:	Absorber(3) - 0.07-0.16 MPa (0-10 psig) PHOSAM stripper(1) - 1.3-1.7 MPa (180-250 psig)
Solution Circulation Rate:	Depends on feed ammonia concentration and pressure of absorber and stripper.

2.5 Process Efficiency and Reliability(1) - On coke oven gases, an ammonia removal of up to 99.7% can be obtained at absorption temperatures of 314°K-333°K (105°F-140°F). Recovered anhydrous ammonia is 99.99% pure. The PHOSAM process has reportedly been in successful operation at U.S. Steel's largest coke plant (in Clairton Works, Pittsburgh, PA) since 1968.

2.6 Raw Material Requirements(1)

H_3PO_4 makeup (as 100% H_3PO_4) - 0.002 kg/kg NH_3

NaOH for ammonia fractionator (as 100% NaOH) - 0.003 kg/kg NH_3

2.7 Utility Requirements(1)

Steam @ 3.7 MPa (550 psig): 12 kg/kg NH_3

Steam @ 0.27 MPa (25 psig): 8 kg/kg NH_3

Cooling water: 300 l/kg (40 gal/lb) NH_3

Electric power: 0.066 kwh /kg NH_3

3.0 Process Advantages

- Commercially available.
- Process recovers anhydrous ammonia.
- Process is efficient at separating ammonia from H_2S and other acid gases in gaseous or wastewater streams.
- Process uses a relatively inexpensive and non-hazardous/non-toxic solvent.
- Process can reduce free ammonia levels in wastewaters to 100-200 mg/l.

4.0 Process Limitations

- Wastewater from the process contains levels of ammonia (~100 ppm) and phosphate (~7 mg/l) which may require further treatment.
- Moderately high steam and cooling water requirements.

5.0 Process Economics

A PHOSAM W plant handling 13.7×10^6 l/day (3.6×10^6 gal/day) of sour water is estimated to have a capital cost of 8.2 million 1976 dollars(3). Operating costs for such a plant are estimated at about \$1/1000 l (\$4/1000 gals). Sale of ammonia can offset about \$0.14/1000 l (\$0.55/1000 gals) for each 1000 mg/l of ammonia in the feed.

6.0 Input Streams

6.1 Sour Water Feed (Stream 1) - No operating data available. The following sour water feed composition and flow rate were submitted to USS Engineers and Consultants by C.F. Braun and Co. requesting design and cost data for coal gasification applications(5):

Component	mg/l
Carbonate CO_2	13,000
Sulfide (as H_2S)	350
HCN	330
NH_3	4,800

Component	mg/l
Phenol	3,500
Flow Rate - l/min (gal/min)	12,540 (3,300)
Temperature	366°K (200°F)

6.2 Low Pressure Steam (Stream 2) - see Section 2.7

6.3 High Pressure Steam (Streams 3 and 4) - see Section 2.7

6.4 Caustic Feed (Stream 5) - see Section 2.6

6.5 Make-up Phosphoric Acid - see Section 2.6

7.0 Intermediate Streams(2)

7.1 Rich Ammonium Phosphate Solution (Stream 7) - Concentration about 40% by weight; salts in solution approximate the formula $(NH_4)_{1.8}H_{1.2}PO_4$. The pH of the rich solution is approximately 6.8.

7.2 Lean Ammonium Phosphate Solution (Stream 8) - Concentration about 40%; salts in solution approximate the formula $(NH_4)_{1.3}H_{1.7}PO_4$. The pH of the lean solution is approximately 5.2.

7.3 Fractionator Bottoms (Stream 9) - Ammonia level is approximately 500 mg/l(1). No other composition data available. Bottoms will be alkaline since caustic is added to enhance ammonia removal and prevent acid gas contamination of product ammonia. This stream is normally recycled to the sour water stripper.

8.0 Discharge Streams(2)

8.1 Product Ammonia (Stream 10) - Anhydrous and approximately 99.99% pure(1). No trace composition data available.

8.2 Purified Gas (Stream 11) - Equilibrium data are proprietary, but UEC reports that normal design allow 0.5% to 0.8% of the free ammonia in the feed water to remain in the purified gas. Acid gases (e.g., CO_2, H_2S, HCN) are almost completely stripped from sour feed water and will be present in purified gas in the same molar ratio as they appeared in the feed to the sour water stripper.

8.3 Stripped Sour Water (Stream 12) - Free ammonia content is approximately 100-200 mg/l(1). Acid gases are essentially completely removed by stripping. Phenols and other organics are only partially removed. Fixed ammonia salts remain in the stripped water unless neutralized by alkali addition.

9.0 Data Gaps and Limitations

Due to the proprietary nature of the process, limited data are available on the properties and flow rates of most streams associated with the PHOSAM W process.

10.0 Related Programs

C.F. Braun, as the evaluation contractor for the ERDA-AGA program on high Btu gas from coal, has obtained designs and data for the application of PHOSAM W to sour waters likely to be encountered in coal gasification(5). Detailed information about this design are not currently publicly available, due to the proprietary nature of the process.

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CHEVRON WWT PROCESS

1.0 General Information

1.1 Operating Principle - Stripping of hydrogen sulfide and ammonia from sour waters with steam in two separate stages to produce gaseous streams suitable for sulfur and ammonia recovery.

1.2 Development Status - Commercially available (first commercial unit was constructed in 1966). Several units are now in operation in refineries in California, Texas, Canada, Japan and Kuwait(4).

1.3 Licensor/Developer - Chevron Research Company
575 Market Street
San Francisco, Calif.

1.4 Commercial Applications - To date, all commercial applications have been for the processing of refinery sour waters.

2.0 Process Information

2.0 Flow Diagram (see Figure E-10) - Degassed sour water is fed to a reboiler stripper column where hydrogen sulfide and carbon dioxide are stripped overhead. Stripper bottoms with the bulk of the ammonia are fed to a second reboiler stripper column (operated under different temperature and pressure) for ammonia stripping. The overhead from the second stripper is scrubbed with cold aqueous ammonia to remove traces of H_2S, and compressed and condensed to form anhydrous or aqueous ammonia; hydrogen sulfide rich aqueous ammonia is recycled to the degasser.

2.2 Equipment - The process employs pressure vessels, distillation columns, scrubbing towers, and compression equipment. Materials used in these equipment are not known.

2.3 Feed Stream Requirements - Process incorporates a degasser for the removal of highly volatile organics. Volatile inorganics (CO_2 and HCN) will appear in the hydrogen sulfide stripper overhead. Phenols

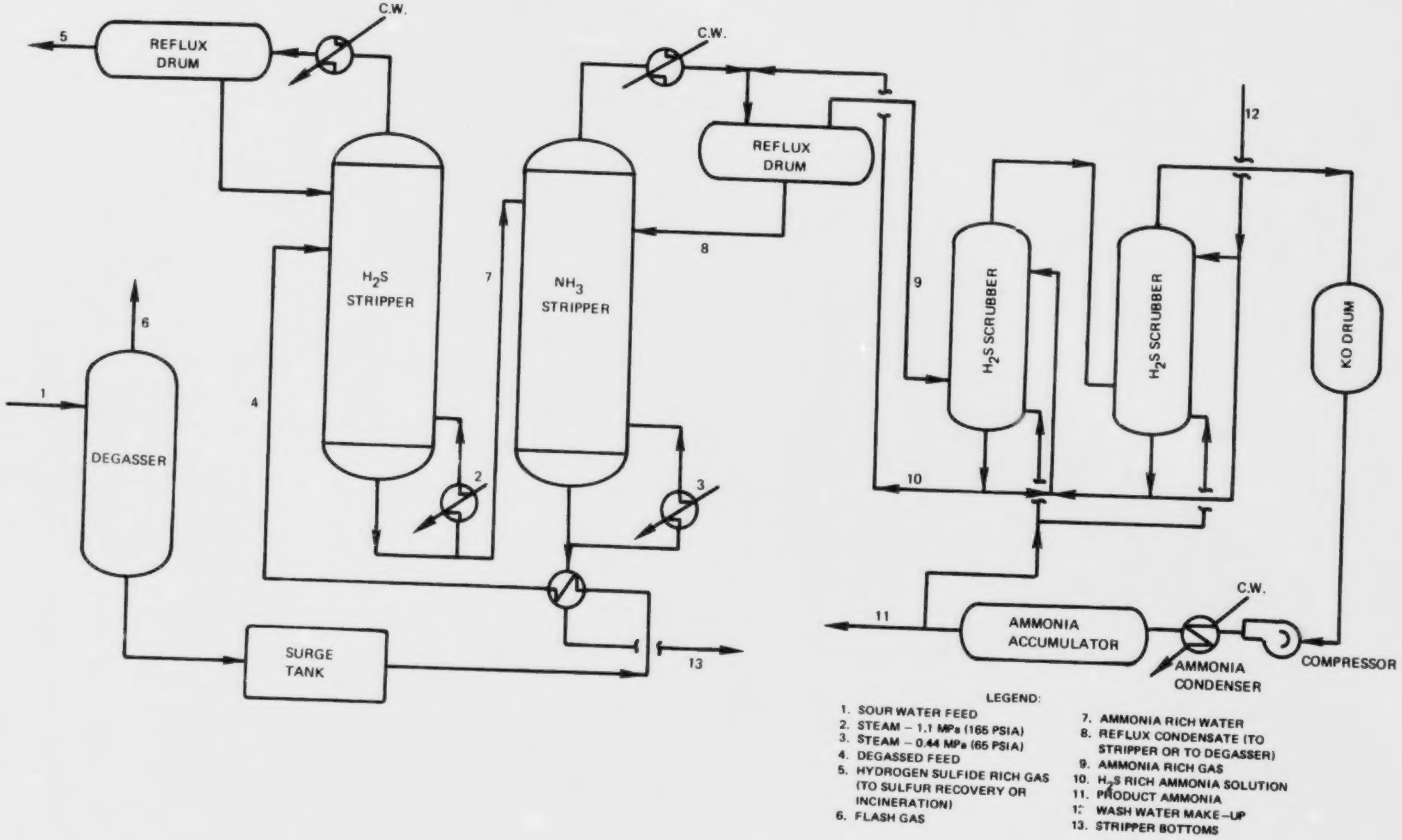
REFLUX DRUM
C.W.
C.W.
REFLUX DRUM
H_2S STRIPPER
NH_3 STRIPPER
DEGASSER
SURGE TANK
H_2S SCRUBBER
H_2S SCRUBBER
KO DRUM
AMMONIA ACCUMULATOR
C.W.
AMMONIA CONDENSER
COMPRESSOR
1
2
3
4
5
6
7
8
9
10
11
12
13
LEGEND:
1. SOUR WATER FEED
2. STEAM – 1.1 MPa (165 PSIA)
3. STEAM – 0.44 MPa (65 PSIA)
4. DEGASSED FEED
5. HYDROGEN SULFIDE RICH GAS (TO SULFUR RECOVERY OR INCINERATION)
6. FLASH GAS
7. AMMONIA RICH WATER
8. REFLUX CONDENSATE (TO STRIPPER OR TO DEGASSER)
9. AMMONIA RICH GAS
10. H_2S RICH AMMONIA SOLUTION
11. PRODUCT AMMONIA
12. WASH WATER MAKE-UP
13. STRIPPER BOTTOMS

Figure E-10. Chevron WWT Process Flow Diagram will appear largely in ammonia stripper bottoms. The process is more economical when applied to feeds containing high levels of hydrogen sulfide and ammonia (3 to 5 wt % each(1)). However, Chevon Research Company has patented a presentation process to handle feeds with low H_2S and NH_3 concentrations(2).

2.4 Operating Parameters(2) - Basis is petroleum refinery design.

Hydrogen Sulfide Stripper

Still bottoms:	Temperature: ? Pressure: ?
Overhead:	Temperature: 311°K (110°F) Pressure: 780 kPa (115 psia)

Ammonia Stripper

Still bottoms:	Temperature: 367°K (200°F) Pressure: 440 kPa (65 psia)
Overhead:	Temperature: ? Pressure: ?

2.5 Process Efficiency and Reliability(1,2) - Process is capable of producing a hydrogen sulfide stream with less than 50 ppm (wt) NH_3; an ammonia stream with less than 50 ppm (wt) H_2S; and a stripped water stream containing less than 50 mg/l ammonia and 5 mg/l sulfide. Reliability of the process is reportedly high. (A Chevron WWT plant in El Segundo, Calif. has operated for several years without a major shutdown.)

2.6 Raw Material Requirements - No raw materials are required for the process.

2.7 Utility Requirements(4) - Based on a design feed for coal gasification application (see Section 6.0)

Total Steam:	1.0 MPa (150 psig) with returnable condensate - 0.16 kg/l (1.31 lbs/gal) feed
Electric power:	0.04 kwh /l (0.01 kwh /gal)*
Cooling water:	0.48 l/l feed

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*Approximately 1/3 of electric power is for ammonia product compression.

3.0 Process Advantages

- Commercially available and has been demonstrated to be reliable.
- Can produce either anhydrous or aqueous ammonia.
- Can produce a concentrated hydrogen sulfide stream suitable for sulfur recovery.
- Achieves low ammonia and hydrogen sulfide levels (50 and 5 mg/l, respectively) in stripped wastewater(2).
- Relatively low cooling water requirements(3).

4.0 Process Limitations

- Process does not remove phenols (or other low volatile organics) from wastewaters.
- Process consumes relatively large amounts of electricity(3).
- Process economics are highly dependent upon plant size, feed ammonia and hydrogen sulfide levels(4).

5.0 Process Economics

A study comparing the economics of the Chevron WWT process with the conventional sour water stripping for application to coal conversion wastewaters has indicated that the capital cost for the Chevron process would be 3.2 million dollars (1975 dollars) higher than that for a conventional steam stripper handling 18 x 10^6 l/day (4.75 mgd) of wastewater(3). This same study indicated annual utility costs of 1.35 million dollars (1975 dollars) for the Chevron plant compared to 1.4 million dollars for the conventional stripper. The ammonia recovered in the above Chevron plant, however, has an estimated annual sales value of 4.65 million dollars (1975 dollars) which significantly offsets the higher capital and utilities costs of the Chevron plant(3).

Chevron Research Company has reviewed and updated the above cost study and has estimated that the installed cost of the 18 x 10^6 l/day (4.75 mgd) plant would be 11 million 1978 dollars(4). This plant includes a preconcentration process to produce a suitable feed to Chevron WWT.

6.0 Input Streams

6.1 Sour Water Feed (Stream 1) - In refinery applications feed water ammonia concentrations have ranged from 12,000 to 55,000 mg/l, sulfide concentrations from 25,000 to 55,000 mg/l as H_2S(1). Levels expected in coal gasification wastewaters are generally much lower. The following feed compositions have been assumed in a design of a Chevron process for application to coal gasification sour water(3,4).

Constituent	Concentration (mg/l)
Carbonate Carbon (as CO_2)	13,000
Sulfide (as H_2S)	230
Cyanide	330
Ammonia	4,800
Phenol	3,500

6.2 Steam (Streams 2 and 3) - see Section 2.7.

6.3 Make-up Wash Water (Stream 12) - No data available.

7.0 Intermediate Streams

7.1 Degassed Feed (Stream 4) - No data available.

7.2 Ammonia Rich Water (Stream 7) - No data available.

7.3 Reflux condensate (Stream 8) - No data available.

7.4 Ammonia Rich Gas (Stream 9) - Contains about 2% (wt) hydrogen sulfide in refinery applications(2). No other composition data available.

8.0 Discharge Streams

8.1 Hydrogen Sulfide Rich Gas (Stream 5) - Product specifications for this stream are less than 50 ppm (wt) ammonia and less than 5000 ppm (wt) water vapor(2). Depending on the composition of the sour water feed, the stream may contain CO_2, HCN, organics, etc. No actual composition data available on this stream.

8.2 Flash Gas (Stream 6) - No data available.

8.3 Stripper Bottoms (Stream 13) - Product specifications for this stream are less than 50 mg/l ammonia and less than 5 mg/l sulfide. No actual composition data available.

A design case for coal gasification wastewater treatment (see Section 6.1) has specified the following composition(3):

Component	Concentration (mg/l)
Carbonate Carbon (as CO_2)	0
Sulfide (as H_2S)	0
Cyanide	17
Ammonia	11
Phenol	2900

8.4 Product Ammonia (Stream 11) - Product specifications for this stream are less than 5 ppm (wt) hydrogen sulfide and less than 1000 ppm water. No other data available.

9.0 Data Gaps and Limitations

Data gaps and limitations for the process relate primarily to the composition of various process and waste streams. Existing applications of the Chevron process have been to refinery sour waters which contain very high levels of ammonia and hydrogen sulfide. Information about process performance in applications to feeds containing lower levels of ammonia and hydrogen sulfide (e.g., sour waters expected in coal gasification) is not publicly available, although Chevron Research has patented a pre-concentration process to handle dilute feeds such as those encountered in coal gasification applications(4).

10.0 Related Programs

C. F. Braun, as evaluation contractor for the ERDA-AGA program on high Btu gas from coal, has obtained designs and data for the application of Chevron WWT to sour waters likely to be encountered in coal gasification(3). Detailed information about this design is not currently publicly available.

No other programs aimed at the evaluation of the applicability of the Chevron process to coal gasification or at environmental assessment of the process are known to be under way or planned.

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Dissolved/Particulate Organics Removal Module

Biological Oxidation
Evaporation/Retention Pond
Chemical Oxidation
Phenosolvan
Activated Carbon Adsorption

BIOLOGICAL OXIDATION PROCESS

1.0 General Information

1.1 Operating Principle - Use of microorganisms to convert organic compounds to carbon dioxide, water and other end products. Air or oxygen is provided for the biological oxidation of organics.*

1.2 Development Status - Commercially available. Numerous units are in operation throughout the world for municipal waste treatment and for treatment of industrial wastes, including coal gasification and petroleum refinery wastes.

1.3 Licensor/Developer - Many biological treatment systems and equipment are offered by numerous suppliers. Some licensed versions of biological processes are patented, such as the UNOX pure oxygen activated sludge technology (Union Carbide Corporation, So. Charleston, West Virginia)(1). A complete listing of these systems is available in the literature (e.g., pollution control editions of ES&T, Pollution Engineering, Chemical Engineering, etc.).

1.4 Commercial Applications - Coal related applications include: (a) SASOL Lurgi-type coal conversion facility, Sasolburg, So. Africa - trickling filters(2); (b) HYGAS pilot plant, Chicago, Illinois - waste stabilization pond(3); and (c) Bethlehem Steel Co., coke plant, Bethlehem, Pa. - commercial scale air activated sludge system(4).

2.0 Process Information

2.1 Flow Diagram (see Figure E-11) - The most widely used biological treatment systems are: (a) activated sludge (air activated and high

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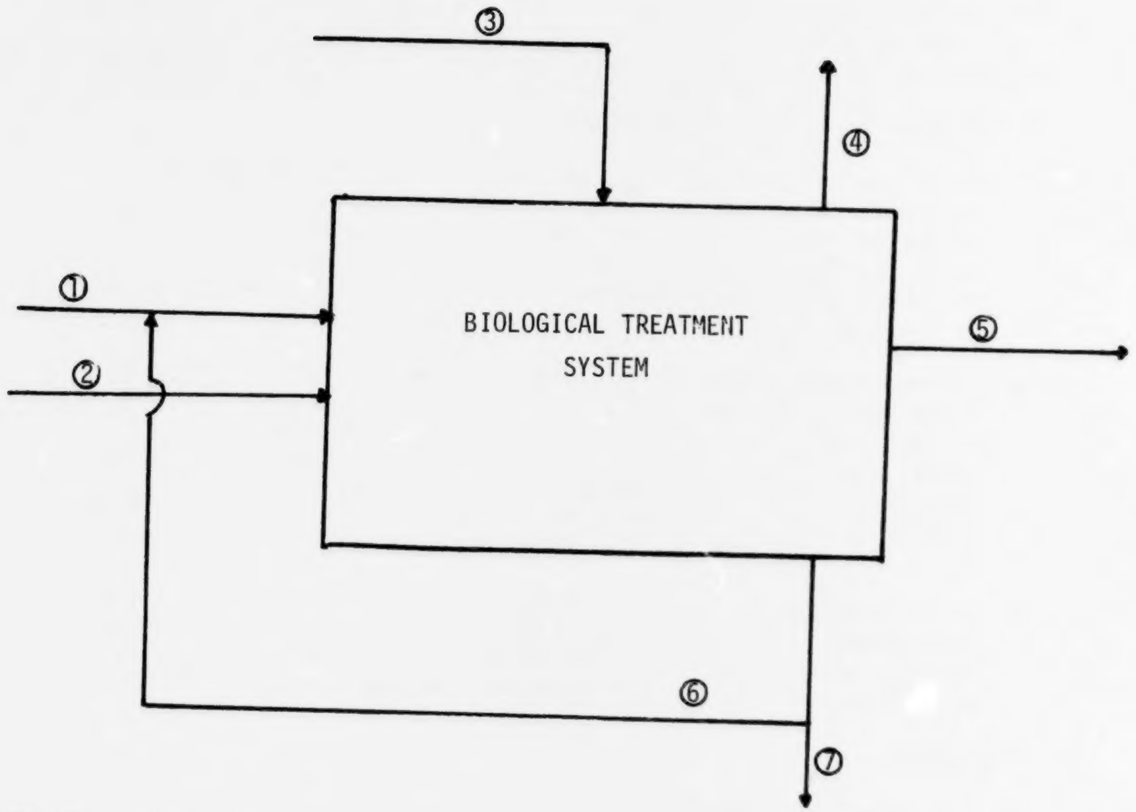
*When air or oxygen are used, the biological oxidation is classified as aerobic oxidation. In the absence of air or oxygen (anaerobic conditions), the decomposition of organics is incomplete and results in the production of intermediate organic compounds, methane, sulfide, etc. Except for certain special applications (e.g., treatment of organic sludge or concentrated waste), aerobic treatment is the system of choice and is discussed in this data sheet.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BIOLOGICAL TREATMENT SYSTEM
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LEGEND:

1. Influent Waste
2. Nutrients/pH Adjustment Chemicals
3. Air or Oxygen
4. Fugitive Emissions
5. Effluent to Clarifier for Solid Separation
6. Sludge to Recycle
7. Excess Sludge to Treatment/Disposal

Figure E-11. Simplified Schematic of Biological Oxidation System(5) purity oxygen activated); (b) trickling filters; (c) lagoons (waste stabilization ponds); and (d) oxidation towers.

- Activated sludge: The conventional activated sludge process consists of a biological reactor unit containing a high concentration of microorganisms. Air or oxygen (Stream 3) is supplied either by mechanical aeration or by a diffused air system. The treated waste is sent to a clarifier for solids/liquids separation. A portion of the settled sludge (Stream 6) is recycled to the biological reactor to "seed" the raw wastewater; the excess sludge (Stream 7) is sent to disposal.
- Trickling Filter: This system consists of a filter bed and wastewater distribution (i.e., sprinkler system) and a sedimentation tank. The filter bed, which is typically 9.3 - 124 m (3-40 ft) deep, consists of rock or synthetic media to which microbial films are attached. Most systems employ recirculation to increase efficiency and minimize shock loadings.
- Lagoons (waste stabilization ponds): These systems consist of large basins ranging from 3.1 to 37.2 m (10-122 ft) in depth and are classified as aerobic, anaerobic or facultative. In aerobic lagoons, air or oxygen is provided through natural surface aeration or by mechanical means (aerated lagoons). In facultative lagoons, both aerobic and anaerobic waste digestion occur (anaerobic conditions exist near the bottom of the pond).
- Oxidation towers: Wastewater is used as make-up water for cooling towers. Biological flocs become established in the system (mostly on the surfaces in the cooling tower) and excess flocs are discharged in the cooling tower blowdown.

2.2 Equipment

- Biological reactor unit (i.e., tank, lagoon, filter bed, tower, etc.)
- Sedimentation tanks for solids/liquids separation (activated sludge)
- Mechanical aerators (aerated lagoons, activated sludge)
- Compressors and air diffusers (activated sludge)
- Pumps (all systems)

2.3 Feed Stream Requirements

- Temperature: Optimum for aerobic biological treatment systems - 20°C to 35°C (60°F to 80°F).
- Biodegradability: The organics to be removed must be biodegradable.

- Loading: Varies with the specific biological system, removal efficiencies desired, and specific design. A raw waste may require either dilution or concentration for effective treatment.

- Inhibitory constituents: Wastes containing high concentrations of chemicals toxic to biological systems (e.g., heavy metals, tars, phenols, ammonia, etc.) cannot be treated effectively. Threshold concentrations reported for phenols, ammonia and chloride are: 500 to 1,000 mg/l(5,6); 1200 to 2000 mg/l(7,8); and 2000 mg/l(8).

- Equalization: Wide fluctuations in wastewater characteristics may be detrimental to biological systems. Equalization may be necessary to achieve uniform waste concentrations.

- pH: Optimum pH is between 6 and 8.

- Nutrients: A BOD:N:P ratio of approximately 100:5:1 is required for biological treatment.

2.4 Operating Parameters - Considerable data are available on biological treatment for petroleum refinery and coal conversion wastes. Typical operating parameters for an activated sludge system for testing coke plant wastes are given in Table E-12. Selected operating parameters and data for a hypothetical design activated sludge system for a coal conversion plant are presented in Table E-13.

2.5 Process Efficiency and Reliability - Efficiency depends upon the type and design of process used, and on the nature of the wastewaters. The chemical nature of the compounds determines their biodegradability. Di- and polyhydric phenols (found in coal gasification effluents) are less completely biodegraded than simple phenols. The biodegradabilities of polyaromatic phenols, and most aromatic and heterocyclic compounds are unknown. Data on biological treatment efficiencies for coal gasification facilities are presented in Tables E-14 and E-18. A COD removal efficiency of 91.7% has been reported for the trickling filters in use for wastewater treatment at the SASOL Lurgi-type coal conversion facility, Sasolburg, South Africa(2). Tables E-12 and E-15 present data on coke plant and petroleum refinery applications, respectively. Biological processes have been widely used and proven highly reliable treatment of range of industrial and municipal wastewaters.

TABLE E-12. OPERATING PARAMETERS AND DATA FROM AN ACTIVATED SLUDGE PILOT PLANT FOR TREATING A PHENOLIC WASTEWATER FROM A COKE PLANT*(7)

Parameter	Parameter Range†
Flow rate, l/min (gpm)	1.5 - 4.6 (0.40 - 1.21)
Phenol, mg/l	3,350 - 3,900
Dilution water,† l/min (rpm)	2.0 - 4.5 (7.6 - 17.0)
Recycle sludge, l/min (gpm)	9.1 - 37.8 (2.4 - 10.0)
Retention time, hr.	1.6 - 4.4
Temperature, °C (°F)	27 - 33 (80 - 92)
pH	6.9 - 7.7
Phenol removed, kg/day/kg sludge in aeration	0.43 - 0.93
Sludge growth, kg/kg phenol removed	0.13 - 0.23
Effluent phenol concentration, mg/l	0.2 - 0.8

*Range for 7 individual measurements.

†Dilution water added to raw waste to lower strength prior to treatment

TABLE E-13. DESIGN AND EXPECTED PERFORMANCE DATA FOR A HYPOTHETICAL HIGH PURITY OXYGEN ACTIVATED SLUDGE (HPOAS) SYSTEM FOR A COAL CONVERSION PLANT(4)*

Influent Waste Characteristics		
BOD_5, mg/l	13,000-18,000	
COD, mg/l	25,000-30,000	
Phenol as C_6H_5OH in mg/l	3,000-5,000	
NH_3 as N, mg/l	290	
Flow, l/day (gal/day)	3.22×10^6 (0.85×10^6)	
Temperature, °C (°F)	26.7 (80)	
Design Parameter or Utility Requirement†		
	Step 1	Step 2
Volume of unit, l (gal)	23.0×10^6 (2.62×10^6)	2.2×10^6 0.57×10^6)
Area of Clarifier, m^2 (ft^2)	198.1 (2,130)	263.7 (2,835)
Retention Time, hrs. (based on feed flow)	74	16
Sludge recycle rate, %Q, l/day (gal/day)	132.3 (35)	132.3 (35)
Mean biomass loading, kg BOD_5/kg MLVSS·day	0.8	0.3
Volumetric organic loading, kg $BOD_5/10^3$ m^3·day	5.84	1.35
Recycle suspended solids, wt %	2.0	2.0

(continued)

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*Based on Hygas plant using lignite feed. The design assumes that the biodegradability of the coal conversion wastes are similar to coke plant wastes.

†Two units ("steps") in series, each consisting of a HPOAS unit and a clarifier.

TABLE E-13. Continued

Design Parameter or Utility Requirement† (Continued)	Step 1	Step 2
Effluent solution BOD_5 mg/l	900	45
Oxygen supplied, kg/day (tons/day)	7.2×10^4 (79.0)	4.2×10^4 (4.6)
Average oxygen utilization efficiency, %	79	80
Electric power for aerators, kw-hr	613	38

*Based on Hygas plant using lignite feed. The design assumes that the biodegradability of the coal conversion wastes are similar to coke plant wastes.

†Two units ("steps") in series, each consisting of a HPOAS unit and a clarifier.

TABLE E-14. ANTICIPATED WASTEWATER COMPOSITIONS AND BIOLOGICAL TREATMENT EFFICIENCIES FOR COAL CONVERSION EFFLUENTS

Wastewater Compounds	Anticipated Untreated Effluent (Stream 1) Concentration Range, mg/l	Anticipated Treated Effluent (Stream 5) Concentration Range, mg/l	Biological Wastewater Treatment Removal Efficiency, %	Ref.
Phenols	1,000 - 10,000	1 - 10	99.9+	11
Aromatic Amines	100 - 1,000	70 - 500	30 - 50	11
Monoaromatic hydrocarbons	10 - 100	9 - 90	40+	11
Thiophenes	1 - 10	---*	---	11
Polycyclic hydrocarbons	0.1 - 1	0.03 - 0.08	30 - 80	11
Thiocyanate	---	1 - 10	---	12
Cyanide	---	1 - 10	---	12
Sulfide	---	0.01 - 0.3	---	12
BOD_5	30,000	50 - 150	99.8+	12
Suspended Solids	---	60 - 200	---	12

*No data available

TABLE E-15. EFFICIENCY OF BIOLOGICAL TREATMENT FOR PETROLEUM REFINERY EFFLUENTS(13)

Biological Treatment Method	Percent Removal*					
	$S^=$	BOD	COD	S. Solids	Oil	Phenols
Activated Sludge	97-100	88-90	60-85	---	---	95-99+
Trickling Filters	---	60-85	30-70	50-80	50-80	---
Waste Stabilization Pond (Aerobic)	---	40-95	30-65	20-70	50-90	---
Aerated Lagoons	95-100	75-95	60-85	40-65	70-90	90-99
Cooling Tower Oxidation (Air Stripping)	---	90+	90+	---	---	99.9

*Thiocyanates are approximately 70% removed by all processes.

2.6 Raw Material Requirements

- Air or oxygen (Stream 3): Varies with the type of biological treatment, waste loading and removal efficiency; for most systems, 0.6 to 1.5 kg O_2/kg BOD_5 removed.
- Nutrients/pH adjustment chemicals (Stream 2): See Section 2.3
- Microorganisms: Some strains of bacteria may be added to improve removal efficiency (e.g., PHENOBAC - a commercially available strain of mutated Pseudomonas sp. for removal of phenols).

2.7 Utility Requirements

- Electricity: Used for driving pumps, compressors, etc., and varies with the specific design and removal efficiency desired. Power requirements for activated sludge and aerated lagoon systems are generally between 0.020 to 0.022 hp-hr/lb BOD (0.006 to 0.0074 kw-hr/kg BOD) removed per day.

3.0 Process Advantage(14)

- Widely used commercial processes for which extensive operating experience is available.
- Relatively inexpensive methods for the removal of biodegradable organics and low levels of certain reduced inorganics (e.g., CN^-, SCN^-, S^-, etc.).
- Minimum maintenance requirements for some of the biological systems (e.g., lagoons, trickling filters).
- Little or no raw materials required except for oxygen and air in the case of activated sludge and aerated lagoon systems, and possibly nutrients, and chemicals for pH adjustment.

4.0 Process Limitations(14,15)

- Ineffective for removal of nonbiodegradable and refractory organics (some of which are present in coal gasification effluents - see Section 2.5).
- Inapplicable when waste contains intolerably high concentrations of toxic materials (e.g., heavy metals, toxic organics, etc.).
- Process is highly sensitive to wide fluctuations in wastewater characteristics (e.g., pH, acidity, and organic and hydraulic loadings).
- Some processes (e.g., conventional activated sludge systems trickling filters), generate sludge requiring further treatment and disposal.

5.0 Process Economics

See Tables E-16 and E-17 for actual and estimated costs.

6.0 Input Streams

6.1 Influent Waste (Stream 1) - Wastewater characteristics vary depending on the source. See Tables E-13, E-14 and E-19 for coal conversion wastewater characteristics. See Table E-20 for listing of chemical classes in coal gasification wastes.

6.2 Nutrients/pH Adjustment Chemicals (Stream 2) - see Section 2.6

6.3 Air or Oxygen (Stream 3) - See Section 2.6 and Table E-15.

7.0 Intermediate Streams

7.1 Fugitive Emissions (Stream 4) - NH_3, H_2S, mercaptans and other malodorous organic compounds may be released during routine operations and especially during upsets. No data are currently available on quantities and characteristics of such emissions.

TABLE E-16. ESTIMATED COST OF HYPOTHETICAL DESIGN HIGH PURITY OXYGEN ACTIVATED SLUDGE SYSTEM FOR A COAL CONVERSION PLANT*(4,16)

Capital Costs	10^6 \$ (1977)
Equalization	1.19
Step 1 HPOAS:	
Oxygenation Basins	1.96
Clarification	0.25
Cooling Tower	0.08
Pumps for Recirculation	0.13
Step 2 HPOAS:	
Oxygenation Basins	0.45
Clarification	0.29
Pumps for Recirculation	0.02
Oxygenation Equipment and Related Instrumentation for Steps 1 and 2†	3.50
Installation and Oxygenation Equipment and Related Instrumentation†	0.32
DAF Thickening	0.54
Vacuum Filtration	0.36
TOTAL	9.09
Operating Costs	**10^6 \$/yr (1977)**
Amortization and other capital-related items at 15% of capital/yr	1.36
Maintenance:	
Concrete work	0.05
Machinery	0.08
Electricity at 2,470 kw‡	0.40
Chemicals:	
Phosphorous	0.32
Oxygen, 295 tons/day at \$14.32/ton	1.40
TOTAL	3.61
TOTAL OPERATING COSTS	0.95 \$/1000 liter (3.61 \$/1000 gal)

*See Table E-13 for waste characteristics, design parameters, and utility requirements.

†Quotation from Union Carbide.

‡Excluding electricity required for oxygen generation.

TABLE E-17. YEARLY COSTS FOR TREATMENT OF 1,000 GPM OF OILY PETROLEUM REFINERY WASTEWATER USING AN ACTIVATED SLUDGE TREATMENT SYSTEM(14)

Cost	Dollar Value ($000)
Investment (excluding land)	1,160
Operating Costs	
1. Power ($0.01/hp)	9.6
2. Maintenance at 4% plant cost	46.4
3. Direct Labor and Overhead	40.0
4. Depreciation at 10% plant	116
5. Insurance and Taxes at 3% plant cost	34.8
6. Chemicals	1.0
	247.8
$/1000 liters ($/1000 gal)	0.13 (0.5)

*All costs are in 1970 dollars.

8.0 Discharge Streams

8.1 Effluent to Clarifier for Solids Separation (Stream 5) - Section 2.5. See Table E-18 for effluent data for Synthane wastes.

8.2 Sludge to Recycle (Stream 6) - Approximately 20% of the BOD removed is discharged as sludge in conventional activated sludge systems. A portion of the sludge is returned to the biological reactor to "seed" the raw wastewater. Sludges contain approximately 2%-5% solids. The chemical composition depends on the influent waste and nature of treatment. Generally, sludges contain biological flocs, heavy metals, undegraded or organic degradation products and inerts. No composition data are available for coal gasification wastes.

8.3 Excess Sludge to Treatment/Disposal (Stream 7) - See Section 8.2.

TABLE E-18. TYPICAL PERFORMANCE OF BIOLOGICAL TREATMENT OF SYNTHANE WASTES*(25)

	Run 1	Run 2
Applied F/M, kg TOC/kg MLVSS-day	0.7	0.2
TOC, mg/l		
Influent	1960	500
Effluent	850	150
TOC Removal, percent	57	70
COD, mg/l		
Influent	5960	1250
Effluent	2030	390
COD Removal, percent	64	69
Phenol, mg/l		
Influent	1205	175
Effluent	25	≤1
Phenol Removal, percent	98	99
MLVSS, mg/l	2750	2520

*Treatment unit was a 7-liter activated sludge bioreactor; hydraulic retention time = 24 hours. Wastewater was generated in the Synthane PEDU at Pittsburgh Energy Research Center.

TABLE E-19. SUMMARY OF CLASSES OF ORGANIC CONSTITUENTS IN COAL GASIFICATION RAW GAS QUENCH CONDENSATES (ALL CONCENTRATIONS IN mg/l)

Constituent Class	Synthane TPR-86(18)	Synthane(19)	Lurgi-Westfield(20)	Synthane(21)	Lurgi-SASOL(22)
Monohydric phenols	1690-9380	5250	1833-4560	4506	2410
Dihydric phenols	*	--†	546-1751	--	7718
Polycyclic hydroxy compounds	90-660	40	--	66	--
Monocyclic n-aromatics	30-580	--	--	46	234
Polycyclic n-aromatics	0-210	--	--	97	--
Aliphatic acids	--	730	--	--	226
Others (i.e., benzofurans, benzofuranols, benzothiophenols, hydroxybenzaldehydes, benzoic acid)	210-580	--	--	--	--

*Dihydric phenols have been identified in the wastes; however, concentrations have not been determined.

†Indicates data not available.

9.0 Data Gaps and Limitations

Limited data are available on the characteristics and biotreatability of wastewaters from commercial coal gasification facilities. Data for pilot facilities may not be representative of those for large scale operations.

10.0 Related Programs

An experimental program to determine the composition, biodegradability and biodegradation kinetics of organics in coal conversion wastewaters is currently underway at the University of North Carolina under an EPA contract(23). Treatability studies, including an assessment of activated sludge, trickling filters and anaerobic treatment methods for coal conversion wastewaters, are currently being conducted by the Environmental Studies Institute, Carnegie-Mellon University, Pittsburgh, Pennsylvania, under contract with DOE(24). Biological treatment of Synthane wastewaters is currently being investigated under PERC sponsorship at the Synthane pilot plant. Limited data from this study have already been published and additional results are anticipated(25).

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EVAPORATION/RETENTION POND(1,2,3)

1.0 General Information

Evaporation/retention ponds or lagoons are natural or man-made basins constructed either by digging out a depression on the land or by erecting dikes. Waste is discharged to the pond and water is allowed to evaporate, thus reducing the waste volume and making room for additional waste. The solids or sludge may be removed and landfilled, or the waste may permanently remain at the pond site.

1.1 Applicability - Method is most suitable when large land areas are available, there is a significant net evaporation rate, and there is little risk of contaminating groundwater.

1.2 Development Status - Evaporation/settling ponds have been used widely for the disposal of municipal and a wide variety of industrial wastes. Ponds are used at the SASOL-Lurgi facility and at all coal gasification pilot plants in the U.S. and have been featured in all proposed commercial scale SNG facilities.

1.3 Operating Parameters - Some operating parameters and design considerations include: available land area, climatic and atmospheric conditions, subsoil permeability and distance to surface/groundwaters, pond depth and volume. Ponds may require lining with clays, plastic or other impervious material to prevent groundwater contamination.

2.0 Advantages

- Method is simple and economical to use.
- Wide variations in waste types and loadings are accommodated.
- Minimal maintenance is required.
- Can generate no effluent streams requiring further treatment or disposal.
- The clarified water may be suitable for recycling to plant.

3.0 Disadvantages

- Adequate protection must be provided against surface and groundwater contamination (e.g., use of liners; diversion of surface runoff, etc.).
- Ponds must be provided with suitable containment mechanisms to prevent overflow due to rainfall accumulation. Operation is dependent on climatological conditions. In areas of heavy rainfall, flood protection equipment may be difficult and expensive to provide.
- Method depends on the availability of adequate land and suitability of climate.
- Leachate and undesirable odors may be generated, depending on the type of waste deposited.
- Pond must be monitored for leachate and for erosion control.
- In nonpermanent sites, the deposited solids must be excavated for ultimate disposal, usually by landfilling.
- Surfaces of ponds used for permanent disposal may require stabilization to prevent erosion by wind and precipitation.
- Ambient air above the pond may pick up low levels of volatile materials from the influent waste.

4.0 Process Economics - Depends on the quantity of waste handled, land area required, the cost of labor and equipment (i.e., drainage pipes, monitoring equipment, etc.). When the climate is suitable and large land areas available, use of evaporation/retention basins can be the most economic method for waste disposal.

5.0 Related Programs(4) - Radian Corporation is about to conduct an EPA-sponsored program to assess state-of-the-art holding pond design, construction and management, and to investigate the interactions of chemicals in coal conversion effluents or clay liners used in holding pond construction.

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CHEMICAL OXIDATION PROCESS

1.0 General Information

1.1 Operating Principle - Use of chemicals (primarily ozone, chlorine, chlorine dioxide, and oxygen/air)* to oxidize phenols, cyanides, sulfides, thiocyanates, refractory organics and other wastewater constituents, and to reduce the COD and BOD of the waste; ozone and chlorine compounds are also used for water disinfection(1).

1.2 Development Status - Commercially available. Numerous units in operation throughout the world for municipal and industrial water and wastewater treatment.

1.3 Licensor/Developer - Many chemical oxidation systems are offered by numerous suppliers. Some licensed or patented versions include the UV-OX process for organics removal(2), the Zimpro unit air oxidation system for wastewater and sludge treatment(3), and processes for air oxidation of sulfidic (including ammoniacal sulfidic) sour waters and sulfidic spent caustics from petroleum refineries (e.g., Sulfox process)(4,5).

1.4 Commercial Applications - Applications include municipal water and wastewater treatment plants, petroleum refineries, coke plants and numerous other industries. Although there have been no commercial or pilot-scale applications to coal gasification wastewaters, laboratory-scale testing of Hygas pilot plant wastes using the Zimpro process has been conducted(3).

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*Numerous other chemical oxidants, such as H_2O_2 and MnO_4^-, have been or are currently being used in water and wastewater treatment. The use of these chemicals has been on a small scale, and they are not considered in this data sheet.

2.0 Process Information

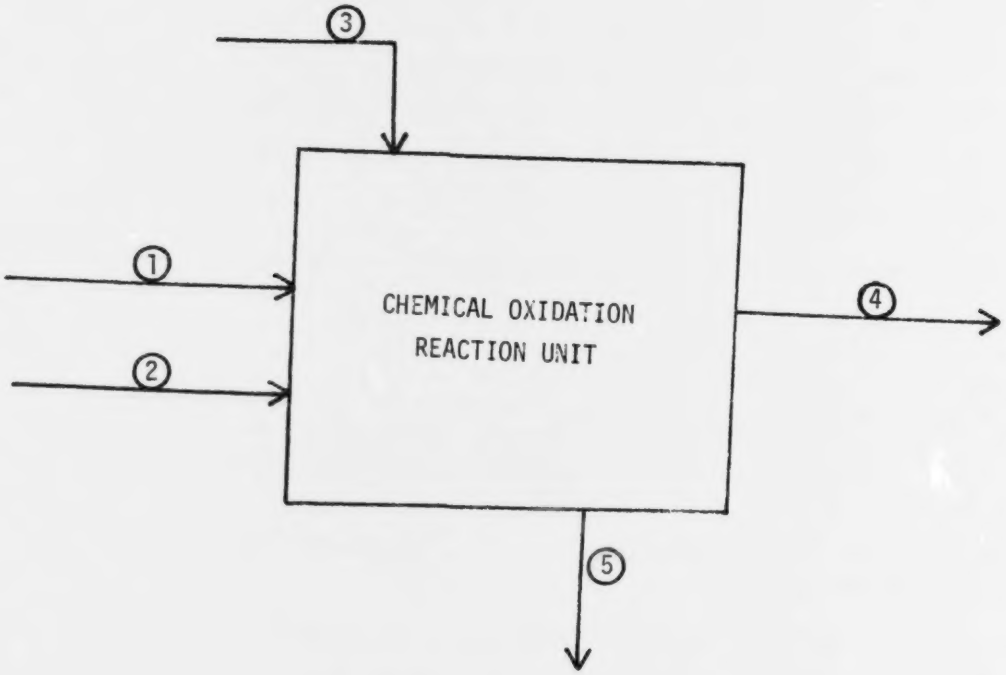
2.1 Flow Diagram (see Figure E-12) - Influent waste (Stream 1) is reacted with a chemical oxidant (Stream 2), under controlled conditions (e.g., temperature, mixing regime, reaction time, etc.) in the reaction unit. Other feed materials (e.g., air, oxygen, etc. - Stream 3), are supplied as required by the specific process employed. Treated effluent (Stream 4) and sludge consisting of reaction products and byproducts (Stream 5) are discharged.

2.2 Equipment

- Chemical oxidation reaction vessel - Design varies with the specific process utilized. Air oxidation of sulfidic sour waters is usually carried out in pressure vessels or multi-stage oxidation towers)(5,8)
- Oxidant source equipment - Varies with the type of process utilized. For ozone oxidation, O_3 generator is required, including air cleaning and drying equipment when the O_3 is manufactured from air.
- Pumps, heat exchangers, mixers, compressors, driers, etc., as required.

2.3 Feed Stream Requirements - Vary with the specific process; many are applicable over wide ranges of wastewater compositions. Most chemical oxidation processes are highly pH dependent; the optimum pH varies with the specific process reactant characterization and reaction time involved (usually 7 or greater for Cl_2). Other important feed variables include temperature (in the case of chlorine, the waste temperature must be below 316°K (110°F) before Cl_2 is added to prevent ClO_3 formation), oxidant concentrations, the presence of inhibitory constituents, and the presence of rate-improving or mechanism-directing catalysts(9).

2.4 Operating Parameters - Temperature, pressure and reaction times vary with the specific waste and process utilized. See Table E-20 for operating parameters of an air oxidation column for sulfidic petroleum refinery wastewaters. Generally 1-2 hours or less reaction time are required for chlorine oxidations(7); less than one hour reaction time is usually required for ClO_2(4).


③
①
②
CHEMICAL OXIDATION
REACTION UNIT
④
⑤

LEGEND:

1. Influent Waste
2. Chemical Oxidant
3. Raw Materials/Additives (air, steam, etc)
4. Treated Effluent
5. Sludge

Figure E-12. Simplified Schematic of Chemical Oxidation Systems

TABLE E-20. OPERATING PARAMETERS FOR AIR OXIDATION COLUMN FOR SULFIDIC PETROLEUM REFINERY WASTES(10)

Parameter	Design Value
Air Flow, m^3/min (ft^3/min)	37.5 (1,325)
Temperature, °K (°F)	366 (200)
Pressure (bottom) psig (atm)	85 (5.8)
Water Flow, 1/day (gal/day)	7.15×10^5 (1.9×10^5)
Air-Water Ratio (approx. inlet conditions), m^3/m^3	9.7
Vessel Volume, m^3 (ft^3)	54.5 (1,925)
$S^=$ in feed, mg/1	8,000
$S^=$ oxidized, tonnes/day (tons/day)	7.6 (8.4)
$S^=$ Oxidation Rate, kg/hr/m^3 (lb/hr/ft^3)	5.8 (0.36)
Excess Air, %*	100

*Basis for oxidation of sulfide to thiosulfate.

2.5 Process Efficiency and Reliability - Efficiency depends on the type and design of process used, and on the nature of the wastewaters. See Tables E-21 through E-23 for efficiencies of: (a) Zimpro wet air oxidation of Hygas pilot plant wastewaters; (b) ozonation of chlorinated hydrocarbons in petrochemical wastewaters; (c) coke plant wastewater oxidation by Cl_2, ClO_2 and O_3; and (d) ozonation of mixed industrial-municipal wastewaters. Efficiencies of removal of contaminants from oil refinery wastes are shown in Table E-24.

TABLE E-21. OPERATING EFFICIENCY FOR ZIMPRO WET AIR OXIDATION OF HYGAS PILOT PLANT WASTEWATERS(3)

Parameter	Feed	694-56-1	% Removal	Sample 694-55-1	% Removal	694-58-1	% Removal
Temperature, °K (°F)	287 (56)	513 (464)	---	553 (536)	---	553 (536)	---
Time, min	---	60	---	60	---	60	---
COD, g/l	13.7	4.9	64.2	3.3	75.9	1.0	92.7
% COD Reduction	---	64.2	---	75.9	---	92.7	---
Total Solids, g/l	1.75	1.36	22.2	1.16	---	2.46	---
Total Ash, g/l	0.36	0.34	5.5	0.37	---	0.38	---
pH	8.2	8.2	---	8.1	---	8.0	---
NH_3 as N, g/l	3.25	2.84	12.6	2.88	11.4	3.07	5.5
TKN, g/l	3.25	3.04	6.5	3.01	7.4	3.29	---
Total S, g/l	0.17	0.13	23.5	0.17	0	0.43	---
Total Halides as Cl, g/l	0.1	0.1	0	0.1	0	0.1	0
Phenol, mg/l	740	<1.0	<0.13	<1.0	0.13	<1.0	0.13
Cyanide, mg/l	0	0	---	0	---	0	---
Thiocynate, mg/l	0	0	---	0	---	0	---
BOD_5, mg/l	---	2350	---	190	---	---	---
Catalyst	---	No	---	No	---	Yes	---

TABLE E-22. COD REMOVAL EFFICIENCIES FOR OZONATION OF PETROCHEMICAL WASTEWATERS(11)*

Ozone Dosage, mg/l	pH Initial	COD, Raw Waste mg/l	COD, Treated Waste, mg/l	% Reduction
994	12.2	3,340	1,410	57.8
2,530	12.6	3,340	900	73
2,700	7.0	3,340	1,460	56.5
3,920	12.6	3,340	745	77.5
4,640	12.6	3,340	450	86.5
5,400	12.6	3,340	413	90.5

*Exact composition of wastewater is unspecified.

TABLE E-23. EFFICIENCIES AND COSTS FOR COKE PLANT WASTEWATER OXIDATION BY Cl_2, ClO_2, AND O_3(12)

Treatment Method	Liquor Treated	Cyanide Concentration, mg/l		Reduction Efficiency, %	Approximate Cost,* \$/million liters (\$/million gal)†
		Influent	Effluent		
Chlorine	Bio-effluent, NH_3 removed	10.0	<1.0	90+	35.9 (9.50)
Chlorine dioxide	Bio-effluent	4.0-5.2	1.8-3.6	30-55	68.0 (18.00)
Ozone	Bio-effluent	2.0-5.0	---	Not Effective	---

*Costs are for chemicals only; plant capital costs are not included.

†In 1969 dollars.

TABLE E-24. EFFICIENCY OF OZONATION OF OIL REFINERY WASTEWATERS(14)*

Parameter	Removal Efficiency, %
BOD	50 - 90
COD	50 - 90
Phenol	80 - 99
Sulfide	80 - 99
Suspended Solids	Not Applicable
Chloride	Not Applicable
Ammonia	10 - 30
Cyanide	80 - 99
Toxicity	Reduced

*Wastewaters are secondary effluents from chemical or biological treatment.

2.6 Raw Materials Requirements

- Chemical oxidant (e.g., oxygen, chlorine, etc.) - Actual quantity varies with the oxidant used and species being oxidized. Some oxidants (e.g., ozone, ClO_2) require on-site generation from chemical elements.
- Chemical additives (e.g., for pH adjustment) - Varies, depending on the optimum pH for oxidation and the wastewater characteristics. (In certain applications, chemical oxidants are combined with activated carbon or other materials which serve as catalysts in the oxidation process and result in more effective BOD and COD removal)(6).

2.7 Utility Requirements

- Electricity - Varies with the specific process used. For O_3 generation, one kwh is required to generate 150g (0.33 lb) O_3(6)
- Stam - Required in air oxidations. See Table E-20 for petroleum refinery application.

3.0 Process Advantages(6,13)

- Effective for removal of refractory organics not amenable to biological treatment and wastes containing toxic chemicals.
- Suitable for treatment of certain organics and inorganics present in municipal and industrial wastewaters (e.g., phenol, sulfide, CN^-, SCN^-, etc.). Some of these constituents will be components of coal gasification effluents.
- Some processes (e.g., air oxidation of sulfidic wastewaters and chlorination) are widely used commercial processes for which extensive operating experience is available.
- Most processes impart no taste or order to the treated water and wastewater.
- Some processes result in the destruction of microorganisms and disinfection of the wastewater being treated.

4.0 Process Limitations(6,14,15)

- Generally applicable to small, concentrated waste streams, usually where biological oxidation is ineffective (e.g., when the wastes contain toxic chemicals or refractory organics).
- Effects of chlorination and ozonation not completely understood. Can result in the production of potentially hazardous substances (e.g., chlorinated hydrocarbons when chlorine compounds are used as oxidants).
- O_3 and ClO_2 are unstable and require on-site generation. Capital costs are modest; operating costs may be high.

5.0 Process Economics

Cost of O_3 oxidation is 0.53-0.79¢/1000 liters (2-3¢/1000 gal) for COD of 10 mg/l based on a 10 MM gpd facility(17). Cost of Cl_2 oxidation of CN^- is about half that for ozone(18). Capital costs for wet air oxidation of industrial wastes at throughputs of 5.7×10^4 to 22.5×10^5 lpd (1.5×10^4 to 6×10^5 gpd) are equal to 2460 $(\text{lpd})^{0.7}$ (650 $(\text{gpd})^{0.7}$)(19). ClO_2 costs approximately \$1.82/kg (\$4/lb). (Note: effective ClO_2:waste ratios are as follows: 1.5 to 1 for phenol; 2.5 to 1 for CN^-; and 4-5 to 1 for sulfide or mercaptans(13).) See also Tables E-23 and E-26 for additional cost data.

6.0 Input Streams

6.1 Influent Waste (Stream 1) - Wastewater characteristics vary depending on the source. See Tables E-21 and E-25 for coal gasification wastewater characteristics.

TABLE E-25. PERFORMANCE OF BENCH SCALE OZONE TREATMENT OF SYNTHANE PROCESS WATER (ALL UNITS ARE mg/l EXCEPT pH AND OZONE RATE)(20)

Constituent/Parameter	Raw Wastewater	Ozone Rate		
		0.3 mg/ml	1.2 mg/ml	3 mg/ml
Phenol	2,320	2,340	2,225	820
Cyanide	2.28	1.31	0.6	10.2
Thiocyanate	418	445	450	240
Ammonia	4,250	4,200	4,010	3,710
COD	17,162	17,062	16,504	10,020
BOD	420	399	340	286
TOC	5,800	5,600	3,800	---
Pyridine and Picolines	---	17	17	9
Lutidines	---	5	6	1
Napthalene and Aniline	---	19	18	3
Toluidines	---	8	5	2
2-Methylnaphthalene and Xylidine	---	10	8	1
2-6-Xylenol	---	23	17	6
Quinoline	---	7	3	2
Phenol and O-cresol	---	2,084	1,990	443
M,p-cresol; 2,3 and 2,5-Xylenol	---	1,527	1,438	308
Methyl quinoline	---	22	24	0
2,3-Xylenol	---	44	44	14
3,5-Xylenol; m,p-ethylphenol	---	333	330	77
3,4-Xylenol	---	102	99	16
3-Ethyl-5-Methylphenol	---	54	55	23
C_3-Phenols	---	26	27	21
4-Indanol	---	47	40	16
Indol	---	55	50	16
pH	9.4	9.4	9.4	8.0

TABLE E-26. ESTIMATED CAPITAL AND ANNUAL OPERATING COSTS OF 37.8 MM LITERS/DAY (10 MM GAL/DAY) OZONE MUNICIPAL WASTEWATER TREATMENT PLANTS, IN THOUSANDS OF 1977 DOLLARS(21)

	Ozone Feed Ratio (mg ozone generated per liter of feedwater)		
Capital Costs	40	75	100
Ozone Generators	$ 440	$ 770	$ 980
Compressors and Driers	112	180	212
Mixers and Pumps	98	98	98
Reactors	200	200	200
Piping and Electrical	230	276	289
Building and Supports	160	170	170
Other	146	146	146
Overhead, Fees and Profit	416	552	628
Total	$1,302	$2,392	$2,723
Operating Costs			
Electric Power	$ 147	$ 208	$ 245
Amortization	128	170	193
Oxygen	37	44	48
Operation and Maintenance	41	47	50
Total	$ 353	$ 469	$ 536
$/1000 gal	9.7	12.8	14.7

6.2 Chemical Oxidant (Stream 2) - See Section 2.6.

6.3 Raw Materials (Stream 3) - See Sections 2.6 and 2.7 and Table E-20.

7.0 Discharge Streams

7.1 Treated Effluent (Stream 4) - Varies with the type of waste treated and nature of the oxidant. Effluent is likely to contain quinones (from oxidation of phenol), cyanates (from CN^- oxidation) and thiosulfates (from sulfides and mercaptans). May also contain chlorinated hydrocarbons and aromatics due to incomplete chlorination, or ozonides and epoxides if ozone was used. See Tables E-21 to E-25 for actual effluent data.

7.2 Sludge (Stream 5) - Some processes generate sludges which may contain, depending on the nature of the waste, heavy metals, nondegradable organics, and inerts.

8.0 Data Gaps and Limitations(22)

Data needed for engineering and cost estimates for a commercial-scale chemical oxidation facility as an alternative to biological oxidation for treatment of coal conversion wastewaters are currently unavailable. For example, the rate and extent of oxidation of polyhydric and substituted phenolics, such as those found in coal gasification wastes, by oxidants such as ozone, are not known. Also, the efficiency of ozonation as a function of pH is not well defined.

9.0 Related Programs

The EPA is currently sponsoring a program in the city of Wyoming, Michigan, to develop an understanding of the effects of ozonated effluents on the environment(23). Other related programs are not known.

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PHENOSOLVAN PROCESS

1.0 General Information

1.1 Operating Principles - Extraction of phenols and other organics from process/waste water using organic solvents.

1.2 Development Status - Commercially available.

1.3 Licensor/Developer - Lurgi Mineralötechnik GmbH
American Lurgi Corporation
377 Rt. 17 South
Hasbrouck Heights, N.J.

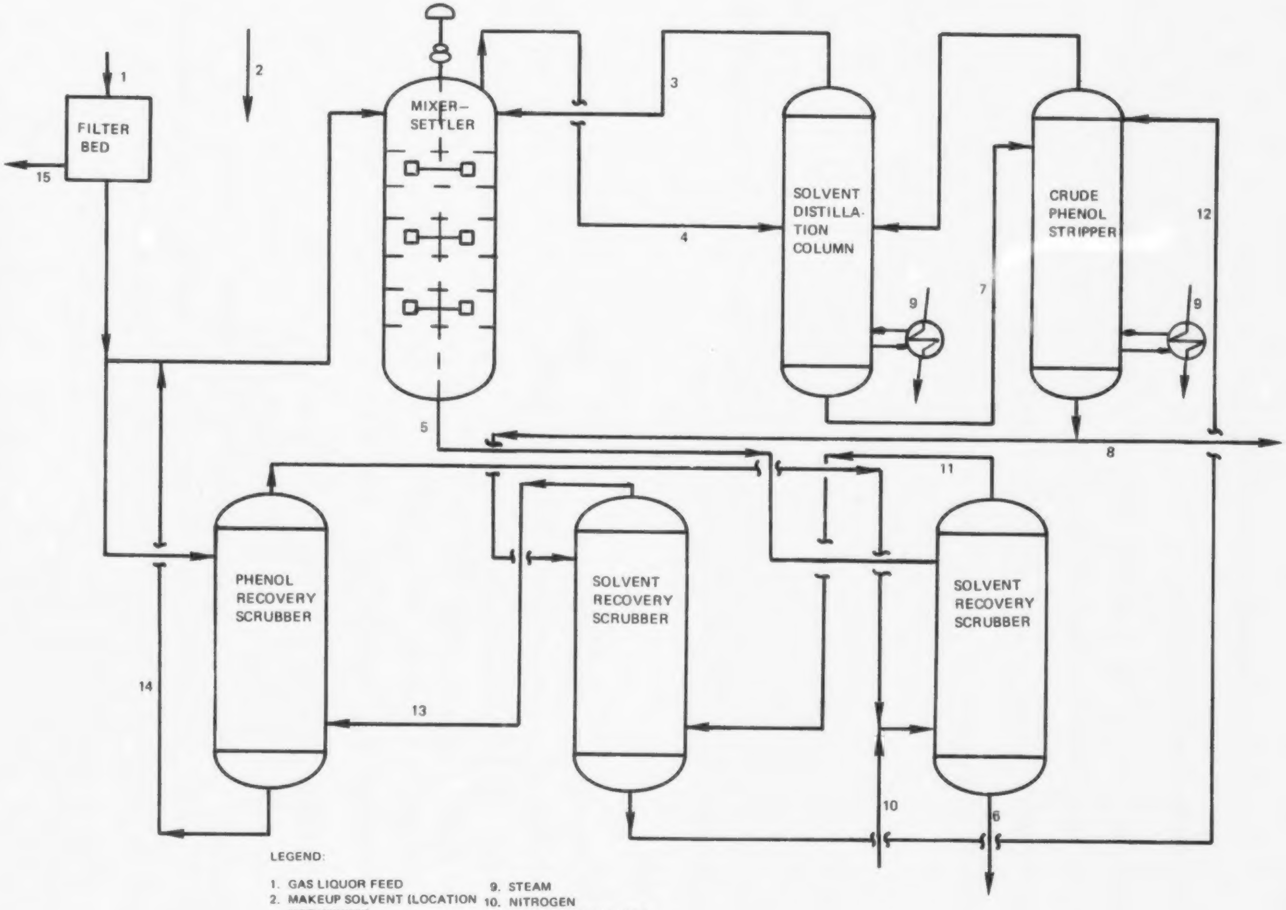
1.4 Commercial Applications(1) - Since 1940 over 30 commercial Phenosolvan plants have been installed worldwide, including plants at Sasolburg, South Africa and Kosovo, Yugoslavia which process waste waters from Lurgi gasification operations.

2.0 Process Information

2.1 Flow Diagram(1) (see Figure E-13) - Filtered phenol containing wastewater is fed to a mixer-settler where it contacts lean organic solvent. After solvent-water phase separation, the solvent is sent to a distillation column for solvent recovery. Lean solvent from the column returns to the mixer-settler while crude phenol is fractionated for purification and additional solvent recovery.

The dephenolized wastewater is stripped of solvent with nitrogen (N_2) gas in a packed tower. Solvent rich N_2 gas is then contacted with scrubbing phenol from the crude phenol stripper to recover most of the solvent. Phenolic vapors remaining in the N_2 gas are then largely removed via contact with a portion of the feed wastewater. Clean N_2 returns to solvent recovery scrubber and the feed wastewater proceeds to the mixer settler.

2.2 Equipment - Filter bed (sand or gravel), mixer-settler, distillation columns, packed towers. All vessels are carbon steel and operate at low pressure.


1
2
FILTER BED
15
MIXER–SETTLER
3
4
5
SOLVENT DISTILLATION COLUMN
CRUDE PHENOL STRIPPER
12
7
9
9
8
11
PHENOL RECOVERY SCRUBBER
SOLVENT RECOVERY SCRUBBER
SOLVENT RECOVERY SCRUBBER
14
13
10
6

LEGEND:

1. GAS LIQUOR FEED
2. MAKEUP SOLVENT (LOCATION NOT KNOWN)
3. LEAN SOLVENT
4. RICH SOLVENT
5. RAFFINATE
6. DEPHENOLIZED GAS LIQUOR
7. CRUDE PHENOL
8. STRIPPED PHENOL
9. STEAM
10. NITROGEN
11. SOLVENT RICH VAPOR
12. RECYCLE PHENOL
13. PHENOL RICH VAPOR
14. RECYCLE GAS LIQUOR
15. FILTER BACKWASH SLUDGE

Figure E-13. Flow Diagram for Phenosolvan Process(1)

2.3 Feed Stream Requirements - Incoming wastewater is commonly filtered to remove suspended solids. Such materials can cause foaming and sludge buildup and can reduce process efficiency if not largely removed prior to the solvent extraction step.

Depending on the solvent used, feed water may require cooling to prevent excessive solvent losses. Generally, the extraction step is conducted at about 300°K-345°K (100°F-160°F).

2.4 Operating Parameters

- Pressure: atmospheric
- Temperature(1,2): 300°K-345°K (100°F-160°F) depending on the solvent.
- Loading(1): weight flow ratio of wastewater to solvent is about 10 for typical designs.

2.5 Process Efficiency and Reliability - A design for a commercial Phenosolvan unit operating on Lurgi gasification wastewater has assumed 99.5% removal of monohydric phenols, 60% removal of polyhydric phenols, and 15% removal of other organics(1). A commercial facility at Sasolburg, South Africa reports >96% total phenol removal(2).

2.6 Raw Material Requirements

- Solvent Properties: Solvents which have been used in Phenosolvan plants include butyl acetate, isopropyl ether, and light aromatic oil(3). Some properties of these solvents are listed below(3,4).

Solvent	Phenol Distribution Coefficient, K_D*	Solubility in Water (wt %)	Boiling Point °K (°F)
Butyl Acetate	49	1.0 at 308°K	398 (256)
Isopropyl Ether	20	0.8 at 308°K	338 (148)
Aromatic Oil	~22	~0.1 at 275°K	353+ (175+)

---

*$K_D = \frac{\text{wt fraction of substance in solvent phase}}{\text{wt fraction of substance in aqueous phase}}$, measured at high dilution

For butyl acetate at 300°K (77°F) the following distribution coefficients for various phenolic compounds have been reported(4):

Compound	K_D
Phenol	65
3,5-xylenol	540
Pyrocatechol	13
Resorcinol	10

- Solvent Makeup Requirements: Makeup is required to balance solvent losses in the crude phenol product and to a lesser extent, in the dephenolized aqueous effluent. The SASOL plant uses about 15 ℓ of butyl acetate makeup per 10^6 ℓ feed(2). No data available for other solvents.
- Nitrogen: No data available.

2.7 Utility Requirements

- Low Pressure Steam(2): 75 kg/1000 ℓ feed (600 lbs/1000 gals)
- Electricity(5): 1-1.7 kwh/1000 ℓ feed (3-6 kwh/1000 gals)
- Cooling Water(2): 5.2 ℓ/ℓ feed

3.0 Process Advantages

- Process can recover phenols suitable for sale.
- Process can achieve 99.5% removal of monohydric phenols and partial removal of polyhydric phenols.
- Process recovers most of the solvent from the dephenolized wastewater via nitrogen purging.

4.0 Process Limitations

- The multivessel operation requires relatively large capital investment.
- Only limited removal of non-phenolic organics is obtained.
- Process uses large amounts of cooling water to effect recovery of phenols and solvent.

5.0 Process Economics

No current data are available on capital and operating costs of commercial operations.

6.0 Input Streams

6.1 Gas Liquor Feed (Stream 1) - see Table E-27

6.2 Makeup Solvent (Stream 2) - see Section 2.6

6.3 Nitrogen (Stream 10) - no data available

6.4 Steam (Stream 9) - see Section 2.6

7.0 Intermediate Streams

7.1 Lean Solvent (Stream 3) - No composition data available; see Section 2.6 for flow rates

7.2 Rich Solvent (Stream 4) - no data available

7.3 Raffinate (Stream 5) - no data available

7.4 Crude Phenol (Stream 7) - no composition data available

7.5 Solvent Rich Vapor (Stream 11) - no data available

7.6 Recycle phenol (Stream 12) - no data available

7.7 Phenol Rich Vapor (Stream 13) - no data available

7.8 Recycle Gas Liquor (Stream 14) - no data available

8.0 Discharge Streams

8.1 Dephenolized Gas Liquor (Stream 6) - No operating data available.

See Table E-27 for properties of a dephenolized effluent following ammonia and hydrogen sulfide removal.

8.2 Stripped Phenol (Stream 8) - No operating data available.

A recent estimate of the gross composition of organics recovered from gas liquor generated by Lurgi gasification of western U.S. coals is(1):

85% monohydric phenols

10% polyhydric phenols

5% other organics

8.3 Filter Backwash Sludge (Stream 15) - no data available.

TABLE E-27. PROPERTIES OF FEED AND EFFLUENT GAS LIQUOR AT THE SASOL PHENOSOLVAN PLANT(2)

Parameter/Constituent	Phenosolvan Feed (mg/l)	Phenosolvan/Stripped Effluent* (mg/l)
Total Phenols	3250 - 4000	160
Steam Volatile Phenols	---	1
COD	---	1126
Fatty Acids (as CH_3COOH)	300	560
Total Suspended Solids	---	21
Total Dissolved Solids	---	875
Suspended Tar and Oil	5000	<21
Total Ammonia	10800	215*
Total Sulfide	228	12*
Cyanide	6	1
Chloride	---	25
Fluoride	---	56
Sodium	53	---
Calcium	---	18
Iron	---	1
Ortho Phosphate	---	2.5
Conductivity (μmhos/cm)	---	1000 - 1800
pH	---	8.4

*Dephenolized gas liquor is steam stripped to remove H_2S and ammonia. The stripping operation is not considered part of the basic Phenosolvan process.

9.0 Data Gaps and Limitations

Data gaps and limitations for the Phenosolvan process relate primarily to the properties of certain process/waste streams. Limited data are available for one coal gasification application of the process which employs butyl acetate as a solvent. No operating data are available for plants using other solvents.

10.0 Related Programs

Radian Corp., under contract to EPA, is conducting an environmental sampling and analysis program at a Lurgi gasification facility at Kosovo, Yugoslavia. This program includes the sampling of gas liquor feed to and effluent from the Phenosolvan plant at this facility. Data are expected to be available in 1978.

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ACTIVATED CARBON ADSORPTION PROCESS

1.0 General Information

1.1 Operating Principle - Removal of organic compounds from a wastewater by adsorption on activated carbon. Methods of contact include: (a) passing the wastewater through a bed of granular carbon and (b) adding powdered carbon directly to treatment systems. In the case of granular carbon, and powder carbon separated from treated water, regeneration is usually effected by thermal treatment. Spend powdered carbon added to biological treatment units usually exits the process as a component of waste sludge and is not reclaimed.

1.2 Development Status - Activated carbon systems are currently employed for both municipal and industrial wastewater treatment. In addition to several existing commercial scale facilities, a number of pilot scale projects in a wide variety of industries are presently underway.

1.3 Licensor/Developer(3,8) - No specific process developer. A number of companies supply activated carbon products and related consultant services. Some of the major vendors include:

Barnebey-Cheney Co., Columbus, Ohio
Calgon Corporation, Catlettsburg, Kentucky
ICI United States, Inc., Marshall, Texas
Husky Industries, Romeo, Florida
Union Carbide Corporation, Carbon Products Division,
    Fostoria, Ohio
Westvaco Corporation, Covington, Kentucky
Witco Chemical Co., Petrolia, PA

1.4 Commercial Applications - Activated carbon systems for wastewater treatment are employed in industries such as coke production, oil refining, petrochemical production, and pesticide manufacture. Carbon systems are also used for trace organics, and taste and odor removal from potable water supplies.

Refineries which have installed activated carbon process for wastewater treatment include Atlantic Richfield, Carson, California, and British Petroleum, Marcus Hook, PA(4). At least one coke plant has tested activated carbon for treatment of wastewater(5).

2.0 Process Information

2.1 Flow Diagram - see Figures E-14 and E-15.

- Granular Activated Carbon systems commonly employ two or more beds.* The series flow Granular Carbon Adsorption system shown in Figure E-14 provides for continuous treatment with periodic removal of one or the other of the adsorbers from service for backwashing and for carbon removal. Backwashing serves to remove particulate matter from the carbon which accumulates over time and increases bed pressure drop.

  In Figure E-15 a typical thermal regeneration process is depicted. Dewatered spent carbon enters the top of a multiple hearth furnace where it travels downward through progressively hotter zones. The furnace provides for: (1) drying, (2) thermal desorption, (3) pyrolysis and carbonization, and (4) gasification. Hot reactivated carbon is quenched and washed to remove fines before return to the adsorption system. Regeneration offgas may be treated by venturi scrubbing (as shown in Figure E-15) or by cyclone and fabric filtration. Incineration may also be required for odor, carbon monoxide, and hydrocarbon emission control. Wastewaters resulting from bed backwashing, reactivated carbon quenching and washing, and venturi scrubbing are usually returned to upstream treatment systems (e.g., solids removal, activated sludge).

- Powdered Activated Carbon may also be employed as an additive to biological treatment systems. In such applications a carbon inventory is maintained by recycle of carbon containing activated sludge and addition of fresh carbon. The carbon contained in excess sludge is not ordinarily recovered. In addition to the feed water, feed carbon, and treated effluent streams, the powdered carbon system would generate a carbon-containing sludge stream.

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*Fixed beds may be arranged in series or parallel with either upflow or downflow design. Pulsed columns with countercurrent flow of carbon and wastewater have also been used. The two bed series system depicted in Figure E-14 is perhaps the most common design and is the only one specifically addressed by this data sheet.

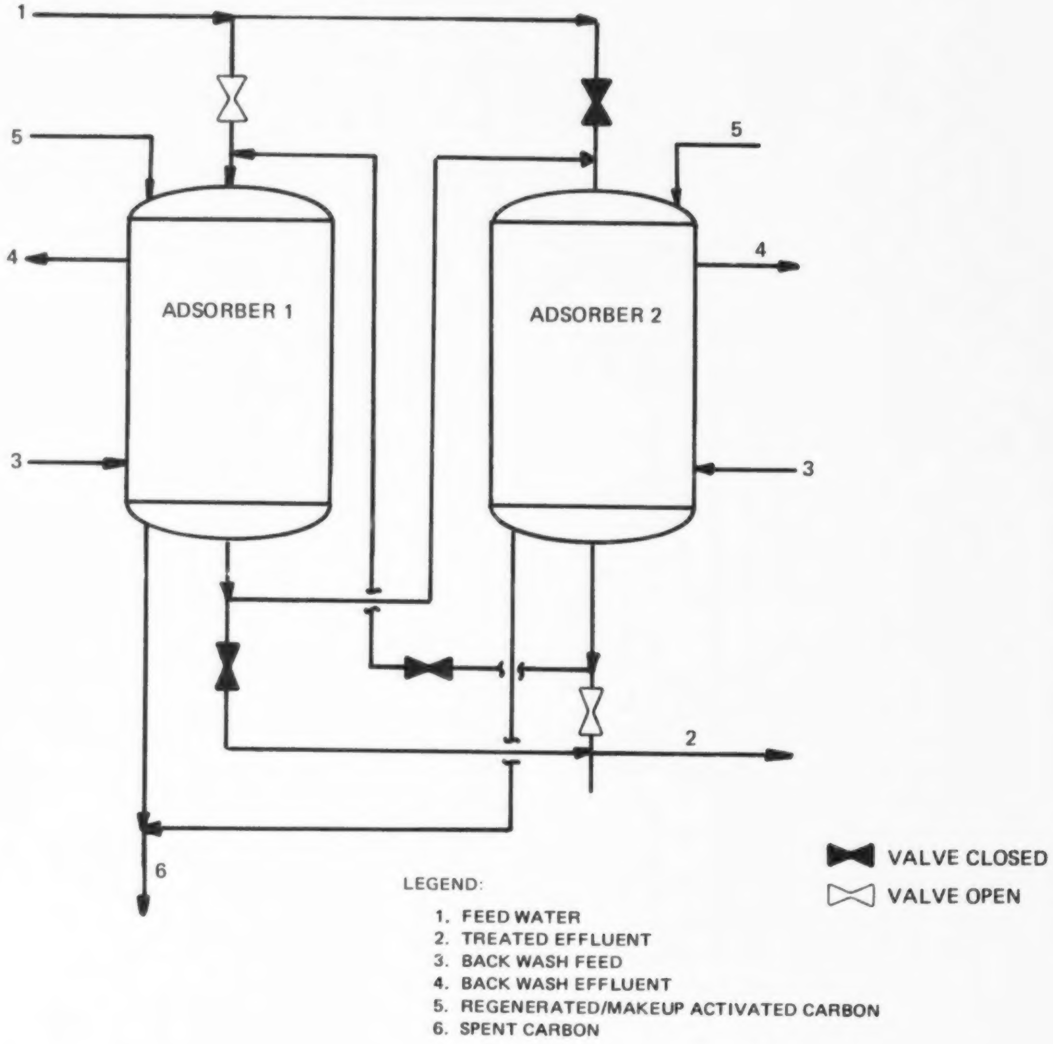
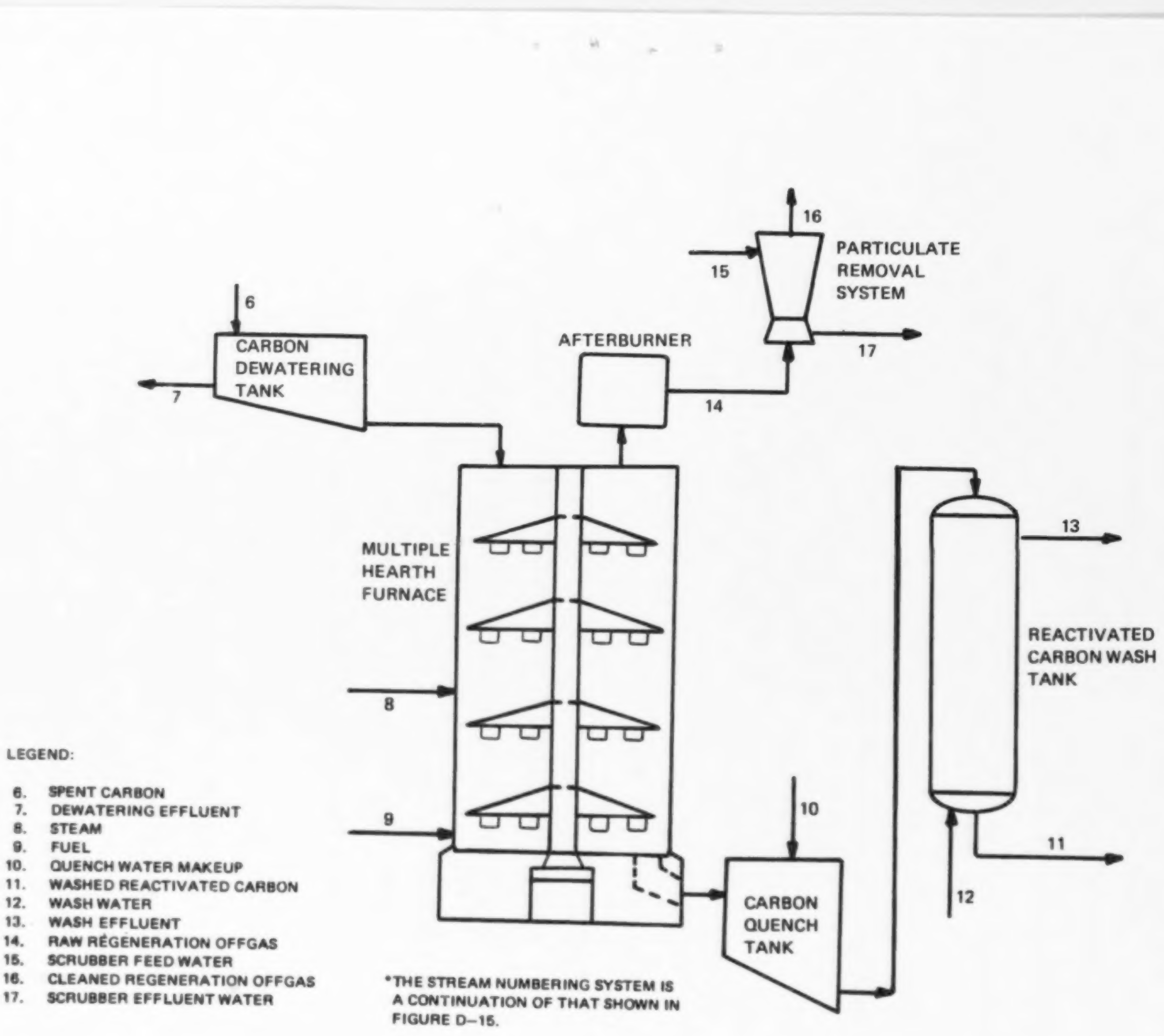

1
5
4
3
ADSORBER 1
ADSORBER 2
5
4
3
2
6
VALVE CLOSED
VALVE OPEN
LEGEND:
1. FEED WATER
2. TREATED EFFLUENT
3. BACK WASH FEED
4. BACK WASH EFFLUENT
5. REGENERATED/MAKEUP ACTIVATED CARBON
6. SPENT CARBON

Figure E-14. Two-Vessel Granular Carbon Adsorption System(1)



16
15
PARTICULATE REMOVAL SYSTEM
17
6
CARBON DEWATERING TANK
7
AFTERBURNER
14
MULTIPLE HEARTH FURNACE
8
9
13
REACTIVATED CARBON WASH TANK
10
11
12
CARBON QUENCH TANK
LEGEND:
6. SPENT CARBON
7. DEWATERING EFFLUENT
8. STEAM
9. FUEL
10. QUENCH WATER MAKEUP
11. WASHED REACTIVATED CARBON
12. WASH WATER
13. WASH EFFLUENT
14. RAW REGENERATION OFFGAS
15. SCRUBBER FEED WATER
16. CLEANED REGENERATION OFFGAS
17. SCRUBBER EFFLUENT WATER
*THE STREAM NUMBERING SYSTEM IS A CONTINUATION OF THAT SHOWN IN FIGURE D–15.

Figure E-15. Multiple Hearth Furnace Carbon Regeneration System(1)

2.2 Equipment(1) - Granular Carbon Adsorption employs carbon steel or concrete vessels and tanks. Corrosion is a big problem but can be minimized by use of coal tar epoxy paints. Pumps and piping for slurry transport are required. A refractory lined multiple hearth furnace is usually required. A venturi scrubber or fabric filter is usually required for furnace particulate control.

2.3 Feed Stream Requirements

Temperature: No specific requirement, hot wastewater feed may lead to gasing in bed and decreased adsorption of organics.

Pressure: No specific requirements.

Composition: Inorganic composition not generally important, except that acidity or alkalinity can influence adsorption efficiency of certain organics (e.g., phenolics, carboxylic acids). Suspended solids (inorganic or biofloc) tend to clog beds and should be largely removed upstream. Periodic bed backwashing is usually required.

2.4 Operating Parameters

2.4.1 Granular Carbon Beds

Adsorption(6,7)

Flow Rate - liters/min/m^2 (gal/min/ft^2): 0.7-3.5 (2-10)

Flow Rate - m/min (ft/min): 0.07-0.4 (0.25-1.34)

Bed Depth - m (ft): 4.5-11.6 (15-38)

Contact Time - min: 15-38 or higher

Contact Time - $m^3/10^3$ l/min (ft^3/gal/min): 15-37 (2-5) or higher

Carbon Capacity - kg COD/kg carbon: 0.2-1.2

Bed Expansion Allowance: 10%-50%

Backwashing(1)

Flow Rate - l/min/m^2 (gal/min/ft^2): 4.2-7.0 (12-20)

Total Flow Requirement: should not exceed 5% of average plant flow

Granular Carbon Regeneration(7,11)

Furnace Temperature: increasing temperature from top to bottom of furnace: 366°K-1255°K (200°F-1800°F)

Oxygen: maintained at less than 1%

Steam: approximately 1 kg/kg carbon

Residence Time: drying - 15 minutes
pyrolysis - 5 minutes
gasification - 10 minutes

2.4.2 Powdered Carbon Addition to Activated Sludge Treatment Systems(9,10)

Steady State Carbon Level in system recovered for maximum efficiency: 200-2000 mg/l or higher (depends upon the nature and strength of wastewater to be treated)

Continuous addition required to maintain needed carbon level: 10-20 mg/l (depends on the wastewater and sludge washing/recycle ratio)

2.5 Process Efficiency and Reliability - Activated carbon preferentially adsorbs high molecular weight and less polar organic compounds. Table E-28 shows the relative adsorbability of several representative compounds as a function of compound type and molecular weight. In actual wastewater applications, a wide range of substances would be encountered and the actual carbon performance would have to be determined by laboratory and pilot testing.

In commercial refinery applications, from 59%-83% COD removal has been obtained with granular carbon systems used without prior biological treatment. A petrochemical pilot plant employing granular activated carbon treatment of activated sludge effluent has achieved 50%-68% COD removal, 53%-80% SOC* removal, and 50%-65% BOD removal(4). Studies of an activated carbon system for treatment of a coke plant effluent after clarification and filtration reported 80% COD removal, 91% TOC removal and 99%+ phenol removal(5).

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*SOC = Soluble organic carbon

TABLE E-28. AMENABILITY OF TYPICAL ORGANIC COMPOUNDS TO ACTIVATED CARBON ADSORPTION*(13)

Compound	Adsorbability† (grams compound/grams carbon)
Ethanol	0.02
2-Ethyl Butanol	0.170
Acetaldehyde	0.022
Benzaldehyde	0.188
Di-N-Butylamine	0.174
Monoethanolamine	0.150
2-Methyl 5-Ethyl Pyridine	0.179
Benzene	0.080
Hydroquinone	0.167
Ethyl Acetate	0.100
Butyl Acetate	0.193
Isopropyl Ether	0.162
Ethylene Glycol	0.0136
Tetraethylene Glycol	0.116
Acetone	0.054
Acetophenone	0.194
Formic Acid	0.047
Valeric Acid	0.159
Benzoic Acid	0.183

*Westvaco Nuchar WV-G (12 x 40 mesh, coal based) carbon

†5g carbon added to 1 liter of solution containing 100 mg/l of compound

In pilot plant granular carbon adsorption tests of biologically treated API separator effluent, 57% BOD removal, 73% COD removal, and 77% TOC removal were achieved(4). Removal of the bulk of Cr, Cu, Fe, and Zn were also observed. Carbon adsorption does not ordinarily remove sulfide, ammonia, or cyanide.

A pilot powdered activated carbon/activated sludge system treating refinery wastewater is reported to achieve 50% suspended solids reduction, 20%-36% COD reduction, and 51%-76% BOD reduction when compared to activated sludge treatment alone(10). Similar results are reported for powdered carbon tests of several other activated sludge systems at refineries(9).

Available information indicates that both granular and powdered carbon systems are reasonably reliable. For effective performance, the systems require routine monitoring of pressure drop, effluent quality, and carbon activity.

2.6 Raw Material Requirements

Properties of Fresh Activated Carbons - Carbons for wastewater treatment applications are usually made from coals. Some properties of commercially available granular carbons are shown in Table E-29(1).

Makeup Requirements(1,9) - Typical losses during thermal regeneration are 5%-10%. Additional losses result from attrition in the handling and transport of carbon and from purposeful withdrawal to minimize ash buildup and to maintain adsorption activity. Exact makeup requirements will depend heavily upon the nature and strength of the wastewater treated, since this determines the frequency conditions of regeneration (see Section 2.4.1).

In the case of powdered carbon, dosage depends upon the nature and strength of the wastewater (see Section 2.4.2).

2.7 Utility Requirements

Electricity: Needed for pumping, carbon reactivation, and control instrumentation. Pumping energy tends to be design specific, but

TABLE E-29. TYPICAL PROPERTIES OF SEVERAL COMMERCIALLY AVAILABLE GRANULAR CARBONS*

Parameter	ICI America Hydrodarco 3000	Calgon Filtrasorb 300 (8 x 30)	Westvaco Nuchar WV-L (8 x 30)	Witco 517 (12 x 30)
Physical Properties				
Surface area, m^2/gm	600-650	950-1050	1000	1050
Apparent density, gm/cc	0.43	0.48	0.48	0.48
Density, backwashed and drained, kg/m^3 (lb/cu ft)	355 (22)	419 (26)	419 (26)	484 (30)
Real density, gm/cc	2.0	2.1	2.1	2.1
Particle density, gm/cc	1.4-1.5	1.3-1.4	1.4	0.92
Effective size, mm	0.8-0.9	0.8-0.9	0.85-1.05	0.89
Uniformity coefficient	1.7	1.9 or less	1.8 or less	1.44
Pore volume, cc/gm	0.95	0.85	0.85	0.60
Mean particle diameter, mm	1.6	1.5-1.7	1.5-1.7	1.2
SPECIFICATIONS				
Sieve size (U.S. std. series)				
Larger than No. 8 (max. %)	8	8	8	†
Larger than No. 12 (max. %)	†	†	†	5
Smaller than No. 30 (max. %)	5	5	5	5
Smaller than No. 40 (max. %)	†	†	†	†
Iodine No.§	650	900	950	1000
Abrasion No., minimum	‡	70	70	85
Ash(5)	‡	8	7.5	0.5
Moisture as packed (max. %)	‡	2	2	1

*Other sizes of carbon available on request from the manufacturer

†Not applicable to this size carbon

‡No available data from the manufacturer

§An index of the amount of pore area in the small molecule size range would be in the range of 0.04 kwh/1000 ℓ (0.15 kwh/1000 gals)(12). Multiple hearth granular carbon regeneration electrical energy ranges from 0.02-0.09 kwh/kg (0.01 to 0.04 kwh/lb) carbon(11).

Steam for Regeneration(11): About 1 kg/kg carbon

Fuel(11): 3300-4400 kcal/kg (6000-8000 Btu/lb) carbon

3.0 Process Advantages

- Commercially proven in a variety of applications.
- Can remove a wide variety of organic compounds to low levels in water, including refractory or non-biodegradable substances.
- Adsorption not generally affected by changes in loading, temperature, or the presence of toxic substances (e.g., Cr, CN^-).
- Adsorbed organics are largely destroyed during thermal reactivation of granular carbon and do not become a sludge disposal problem as in some of the other organics removal technologies.
- Can be used in conjunction with copper addition to remove cyanide via catalytic oxidation(5,14).
- Powdered carbon improves the settleability of solids in activated sludge systems in addition to enhancing organics removal.
- Powdered carbons and, to a lesser extent, granular carbons can provide greater removal efficiencies than calculated from simple adsorption tests due to biological activity promoted on the carbon surfaces.
- Potential for product recovery (e.g., phenols via caustic extraction).

4.0 Process Limitations

- Process is relatively expensive compared to biological oxidation on a weight COD or BOD removal basis. Carbon systems are usually only economical for tertiary treatment applications or where the wastewater is not amenable to biological treatment.
- When thermal reactivation is practiced, potentially valuable organics are not recovered (e.g., phenols).
- Offgas from carbon regeneration often contains particulate matter, carbon monoxide, and unburned hydrocarbons which must be removed prior to atmospheric discharge.
- Trace constituents such as ammonia, cyanide, sulfide, and certain trace elements are not generally removed by activated carbon.
- Sulfide levels may increase during activated carbon treatment due to biological activity. This may lead to odor or effluent problems.

5.0 Process Economics

Capital and operating costs of granular carbon systems depend upon the specific design and the nature and volume of the wastewater treated. One estimate of 1976 capital costs are as follows(7):

Adsorption Equipment

Flow	Cost ($)
4×10^5 ℓ/day (1×10^5 gal/day)	180,000
4×10^6 ℓ/day (10^6 gal/day)	550,000

Regeneration Equipment

Carbon Usage Rate	Cost ($)
910 kg/day (2000 lbs/day)	270,000
8200 kg/day (18000 lbs/day)	1,000,000

1976 operating costs have been estimated at about $0.68 per 1000 liters (400 gals) for every 1000 mg/l of COD removed(12).

6.0 Input Streams

6.1 Feed Water (Stream 1) - See Section 2.5 and Tables E-30, E-31, and E-32.

6.2 Regenerated/Makeup Activated Carbon (Stream 5) - See Table E-29 for typical characteristics of fresh carbon. Regeneration of carbons tends to cause an increase in the average "pore" size and thus reduce carbon affinity for small molecules (e.g., phenol). However, lignite-derived carbons do not undergo as much pore size enlargement as bituminous-derived carbons (see Section 2.6). Regenerated carbon loading capacity for organics tends to be lower than fresh carbon and ash tends to build up since some of the original carbon is burned during each regeneration.

6.3 Backwash Feed (Stream 3) - Typically treated effluent is used for backwashing.

TABLE E-30. PERFORMANCE OF A GRANULAR ACTIVATED CARBON SYSTEM TREATING COKE PLANT WASTEWATERS*(5)

Parameter	Feed Wastewater (mg/ℓ)†	Treated Wastewater (mg/ℓ)†	Average Spent Carbon Loading (%)
Total Suspended Solids	<5	<5	
Total Dissolved Solids	--	--	
Total Organic Carbon	1750	156	
Soluble Organic Carbon	1750	156	30
Chemical Oxygen Demand	6340	1260	
Biochemical Oxygen Demand	--	--	
Phenols	1950	<0.1	25
Cyanide	0.01	0.01	
Ammonia	4000	4000	
Thiocyanate	700	<700	
pH	8.0	8.0	

*Wastewater has received clarification/filtration treatment

†Except pH

6.4 Quench Water Makeup (Stream 10) - Typically treated effluent would be employed.

6.5 Wash Reactivated Carbon (Stream 11) - See Section 6.2. Washing removes some of the loose or brittle material.

6.6 Wash Water (Stream 12) - Typically, treated effluent would be employed.

6.7 Scrubber Feed Water (Stream 13) - No operating data available; this stream would likely be treated effluent.

TABLE E-31. COMPARISON OF GRANULAR ACTIVATED CARBON ADSORPTION AND BIOLOGICAL TREATMENT OF REFINERY WASTEWATERS*(4)

Constituent/ Parameter†	API Separator Effluent	Carbon Treated Effluent	Biologically Treated Effluent	Biological/ Carbon Treated Effluent
BOD	97	48	7	3
COD	234	103	98	26
TOC	56	14	30	7
Oil and Grease	29	10	10	7
Phenols	3.4	0.004	0.01	0.001
Cr	2.2	0.2	0.9	0.02
Cu	0.5	0.03	0.1	0.05
Fe	2.2	0.3	0.2	0.2
Pb	0.2	0.2	0.2	0.2
Zn	0.7	0.08	0.4	0.15
$S^=$	33	39	0.2	0.2
NH_3	28	28	27	27
CN^-	0.25	0.2	0.2	0.2

*Pilot scale operation

†All units are mg/l

TABLE E-32. PERFORMANCE OF POWDERED ACTIVATED CARBON ADDITION TO ACTIVATED SLUDGE SYSTEM*(10)

	Carbon Dose (mg/1)	Flow Rate 1/min (gal/min)	Total Suspended Solids (mg/1)		% TSS Reduc-tion	COD (mg/1)		% COD Reduc-tion	BOD (mg/1)		% BOD Reduc-tion
			Influent	Effluent		Influ-ent	Efflu-ent		Influ-ent	Efflu-ent	
Trial 1											
Control	0	2370 (630)	--[†]	115	--	459	170	--	152	15	--
Carbon Added	24	2370 (630)	--	50	56	457	135	20	213	13	2
Trial 2											
Control	0	2460 (650)	--	164	00	343	266	--	152	30	--
Carbon Added	19	2490 (660)	--	72	55	444	183	30	227	14	52
Trial 3											
Control	0	3180 (840)	--	79	--	367	166	--	188	12	--
Carbon Added	9	3030 (800)	--	42	49	379	112	36	207	3	76

*Treating API Separator wastewater; steady state aeration system contained 450 mg/1 carbon and steady state recycle system contained 1000 mg/1 carbon

[†] -- Indicates data not available

7.0 Process Discharge Streams

7.1 Treated Effluent (Stream 2) - See Tables E-30, E-31, and E-32, and Section 2.5.

7.2 Back Wash Effluent (Stream 3) - No data available. This effluent would normally be returned to upstream suspended solid removal operations.

7.3 Spent Carbon (Stream 6) - Limited actual data are available. Table E-28 shows the capacity of an example carbon for various compounds. The exact loading and nature of adsorbed organics depends upon the wastewater being treated (see Section 6.2).

7.4 Dewatering Effluent (Stream 7) - No data available. This stream would normally be returned to upstream treatment units.

7.5 Washed Reactivated Carbon (Stream 11) - No actual data available. See Section 6.2.

7.6 Wash Effluent (Stream 13) - No data available. This stream would normally be returned to upstream treatment units.

7.7 Raw Regeneration Offgas (Stream 14) - No data available. This gas will contain organics, carbon monoxide, and entrained particulates.

7.8 Cleaned Regeneration Offgas (Stream 16) - No data available.

7.9 Scrubber Effluent Water (Stream 17) - No data available. This stream would normally be sent to upstream dissolved solids removal units.

8.0 Data Gaps and Limitations

Data gaps and limitations relate primarily to the properties of various processes streams associated with activated carbon systems. Carbon adsorption has never been employed for organics removal from coal gasification wastewaters and hence no operating data exists. Data from coke plant and refinery applications are limited and do not necessarily represent a spectrum of organic substances similar to that likely to be encountered in coal gasification. Also, for existing carbon adsorption systems, essentially no information is available for regeneration offgases and backwash waters. Finally, little is known about the nature of organics which remain in the treated effluent from carbon adsorption systems (e.g., biodegradability, toxicity).

9.0 Related Programs

No programs are known to be underway or planned which are specifically aimed at the environmental assessment of carbon adsorption in coal gasification applications. However, as part of the ongoing work with the Synthane PEDU at the Pittsburgh Energy Research Center, the treatability of Synthane wastewaters is being investigated(15). One aspect of this work involves bench scale adsorption tests of biologically treated effluent using Synthane char (physically and chemically similar to commercial activated carbons).

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Sludge Treatment Module

Gravity Thickening
Centrifugation
Vacuum Filtration
Drying Beds
Emulsion Breaking

GRAVITY THICKENING PROCESS

1.0 General Information

1.1 Operating Principle - Removal of excess water from sludges to reduce their volume and to increase solids concentration, using gravity settling.

1.2 Development Status - Commercially available. Numerous units are in operation throughout the world for municipal and industrial sludge thickening.

1.3 Licensor/Developer - Gravity thickener systems and equipment are offered by many suppliers. Listings of the suppliers are presented in technical and trade journals (e.g.. Reference 1).

1.4 Commercial Applications - Gravity thickening is in widespread use in municipal and industrial waste treatment plants. At the SASOL gasification plant in South Africa, gravity thickening is used to concentrate sludge resulting from wastewater treatment(2).

2.0 Process Information

2.1 Flow Diagram (see Figure E-16) - The thickening is carried out (usually in a circular tank) on a batch or continuous basis. In circular tank designs, the influence sludge is distributed at the center of the tank, the clarified liquid is collected at the surface near the periphery and the concentrated sludge is withdrawn at the bottom. The tank is usually equipped with a gently rotating agitator with a sludge scraping mechanism to increase thickening efficiency and to divert the settled sludge to the sludge hopper at the bottom for removal.

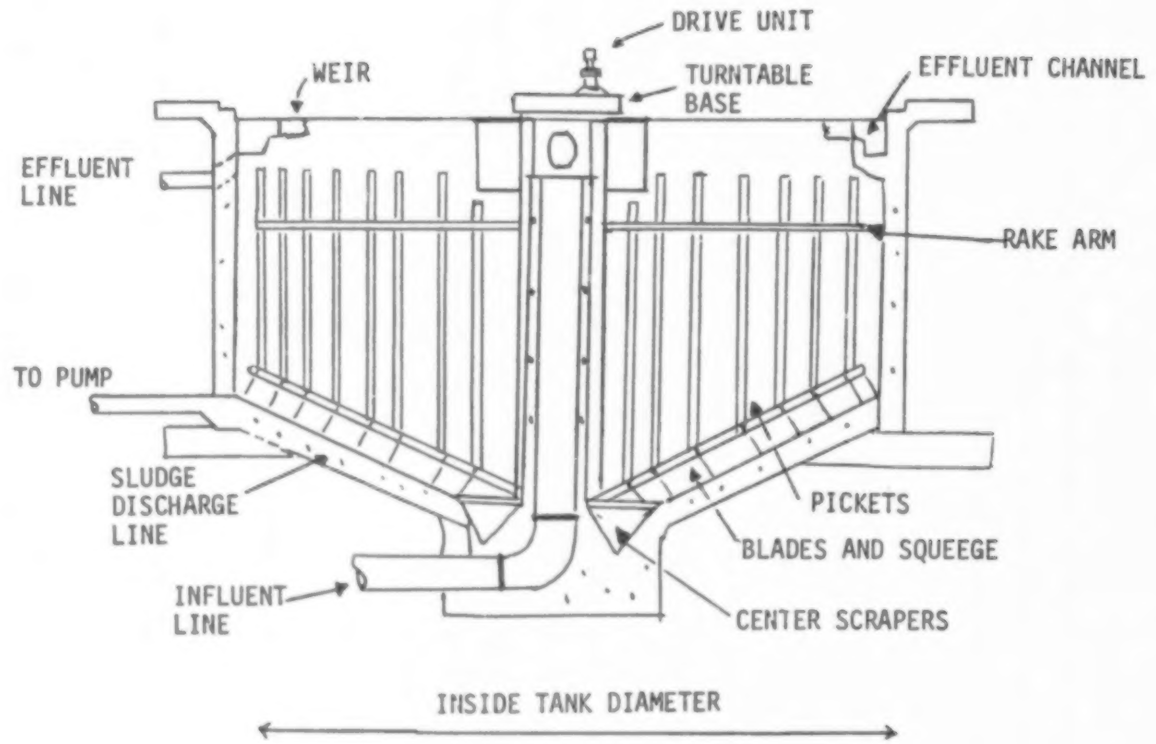
DRIVE UNIT
WEIR
TURNTABLE BASE
EFFLUENT CHANNEL
EFFLUENT LINE
RAKE ARM
TO PUMP
SLUDGE DISCHARGE LINE
PICKETS
BLADES AND SQUEEGE
INFLUENT LINE
CENTER SCRAPERS
INSIDE TANK DIAMETER

Figure E-16. Schematic of Gravity Thickener and Section of Tank(3)

2.2 Equipment - Thickening tank and associated mechanical devices (mixer, drive unit, sludge influent and withdrawal structures, pumps, etc.); the surface area (hence the diameter of the tank is dictated by the design surface area loading, see Section 2.4); tank depth is generally in the 3.0-7.5 m (10-25 ft) range(3).

2.3 Feed Stream Requirements - Good settleability and relatively high solids content are primary requirements for effective thickening. The solids in the sludge would be sufficiently compressible and porous to permit escape of water(3).

2.4 Operating Parameters

- Surface area loading - Determines tank surface area. Varies with the waste and solid concentrations and underflow concentrations desired. Ranges from 118-1301 kg/m^2 (day) (5-55 lb/ft^2 (day)) have been reported(4).

2.5 Process Efficiency and Reliability - The levels of sludge concentration achieved depends on the characteristics of the raw sludge and the thickener design. For waste activated sludges with a solids loading of 142-237 kg/m^2 (day) (6-10 lb/ft^2 (day)), waste underflow concentrations of 5%-8% solids are typically achieved(5).

2.6 Raw Materials Requirements - When sludge requires preconditioning to improve settleability, chemical coagulants (i.e., ferric chloride, aluminum chlorhydrate) may be required.

2.7 Utility Requirements

- Electricity (for control drive mechanism, pumps, raking mechanism, etc.) - Requirements are design-specific.

3.0 Process Advantages(3,6)

- Widely used commercial process for which extensive operating experience is available.
- Little maintenance required.
- Little or no raw materials required except for preconditioning chemicals.

4.0 Process Limitations(3,4)

- Not all sludges can be thickened efficiently by gravity thickening. In certain cases, preconditioning may be required (see Section 2.6).
- Laboratory/bench-scale tests may be required to define sludge thickening characteristics and to generate basis for thickener design.
- For highly biodegradable sludges, long solids retention time may lead to the production of odor and floating sludge.

5.0 Process Economics

For many sludges, thickening is considered to be the most economical way of effecting major sludge volume reduction(3). The capital cost of sludge thickeners has been estimated as(7):

$$\text{Capital Cost (\$)} = (18.8 + 9.1/\exp\,[\text{SAT}/13{,}300]) \cdot (\text{SAT})$$

where SAT = surface area of thickener (ft^2).

6.0 Input Streams

6.1 Influent Sludge (Stream 1) - Typical influent streams include primary and secondary sludges and chemical sludges (e.g., alum, line); solids concentrations of these sludges vary from less than 1% to as much as 60%(4).

7.0 Discharge Streams

7.1 Clarified Effluent (Stream 2) - Consists of wastewater containing some suspended solids.

7.2 Thickener Underflow (Stream 3) - Consists of the thickened sludge; solids concentration depends on thickener loading and influent sludge characteristics.

8.0 Data Gaps and Limitations

No data available on the thickeners used in the SASOL plant for handling sludges originating from coal gasification and associated operations.

9.0 Related Programs

Not known.

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CENTRIFUGATION

1.0 General Information

1.1 Operating Principle - Physical liquids-solids separation by means of sedimentation and centrifugal force.

1.2 Developmental Status - Commercially available. Numerous units are in operation throughout the world in industrial applications and for municipal and industrial waste treatment, including petroleum refinery sludges.

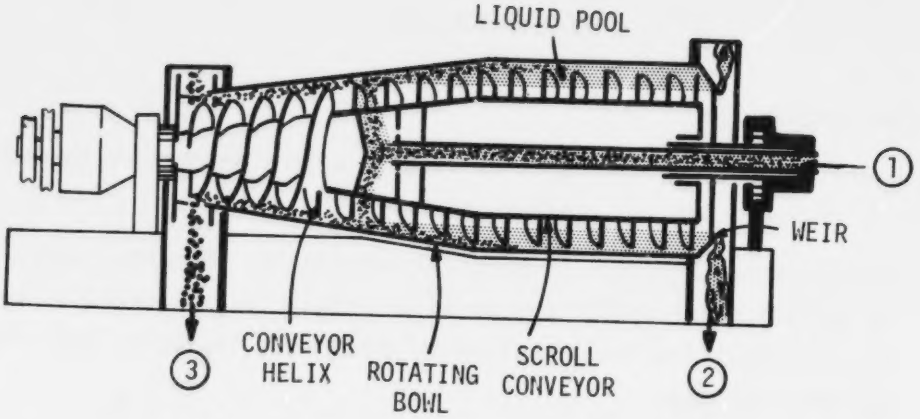
1.3 Licensor/Developer - Many centrifuge treatment systems and equipment are offered by numerous suppliers. A complete listing of these systems and their applications is available in the literature (e.g., Ref. 1).

1.4 Commercial Applications - Method is in widespread use in municipal wastewater treatment(2). Has also been used in treatment of refinery wastes, including oily sludges such as storage tank and gravity separator bottoms(3). Sometimes used to dewater sludges following treatment by coagulation-flocculation or emulsion-breaking techniques. No known applications to coal gasification wastes.

2.0 Process Information

2.1 Flow Diagram - See Figure E-17

- Process Description - Influent wastewater (Stream 1) is fed through a stationary feed pipe into the centrifuge from which it is thrown out through feed parts into the conveyor hub. The solids (Stream 3) are settled out against the outer "bowl" wall by centrifugal force, and are continuously conveyed by a screw moving at a speed slightly different than the bowl to the end of the centrifuge and discharged. A pool volume is maintained in the equipment. Liquid effluent (Stream 2) discharges out of adjustable effluent ports or weirs after passing the length of the pool under centrifugal force.


LIQUID POOL
①
WEIR
③
CONVEYOR HELIX
ROTATING BOWL
SCROLL CONVEYOR
②

Legend:

1. Influent Wastewater/Sludge
2. Liquids Discharge (centrate)
3. Dewatered Solids

Figure E-17. Schematic of Continuous Solid Bowl Centrifuge(4)

2.2 Equipment

- Centrifuge equipment - solid bowl, basket, nozzle, or disk types.
- Pumps

2.3 Feed Stream Requirements(4) - The dewaterability of sludges by centrifugation depends on factors such as the concentration, size, shape, and surface characteristics of the sludge particles, the extent of aggregation, the structural characteristics of the particles, and the viscosity, ionic strength, and pH of the suspending water. Performance parameters which reflect the combined influence of these variables and which are calculated from measurable variables for determination of optimum operating conditions for a given centrifugation system are the specific resistance and the coefficient of compressibility of the waste. Pre-treatment of the sludge by coagulation-flocculation, emulsion breaking and thickening techniques may facilitate centrifugation operations.

2.4 Operating Parameters(4,5) - See Table E-33 for listing of operating parameters and their effect on percent solids recovery and cake solids concentration.

2.5 Process Efficiency and Reliability(4) - Efficiency depends on the type and design of the system used, and on the nature of the sludge treated. Tables E-34 and E-35 present the results of centrifugation of various industrial and municipal sludges. Centrifugation processes have been widely used and proven highly reliable for treatment of a range of sludges.

2.6 Raw Materials Requirements

- Sludge conditioning chemicals (e.g., chemical flocculants) - May be required to enhance removal of fine, difficult-to-remove solids. See Table E-35.

2.7 Utility Requirements

- Electricity - used for driving pumps and central screw feed mechanism. Requirements vary with the specific design and removal efficiency desired.

TABLE E-33. EFFECT OF AN INCREASE IN VARIOUS CENTRIFUGATION VARIABLES ON SOLIDS CAPTURE AND DEWATERING(4)

Variable Parameters	Effect of Increase in Variable On	
	% Solids Recovery	Cake Solids Concentration
Machine Parameters		
Bowl Speed	Increase	Increase
Pool Depth	Increase	Decrease
Scrolling Speed	Decrease	Decrease
Process Parameters		
Feed Rate	Decrease	Increase
Feed Concentration	Decrease	Increase
Temperature	Increase	Increase

3.0 Process Advantages(4,7)

- Simple to operate; units are compact and require little space.
- Totally enclosed to minimize odor dispersion.
- Minimal to nil raw materials requirements.
- Suitable for treatment of a wide variety of sludges with differing physical and chemical properties.
- Minimal supervision requirements.
- Operation can be adjusted to permit concentration of relatively volatile material in sludge in the centrate and concentration of nonvolatile solids in the dewatered solids, thus permitting some selectivity in waste segregation.

TABLE E-34. RESULTS OF CENTRIFUGATION OF SLUDGES(6)

Type of Sludge	Cake Concentration (% Solids)	Solids Recovery (%)		Cost of Chemicals, \$/tonne (\$/ton) of Dry Solids
		Without Chemicals	With Chemicals	
Raw Primary	28-35	85-90	>95	3.3-8.8 (3-8)
Digested Primary	25-35	80-90	>95	3.3-8.8 (3-8)
Activated	6-10*	-	-	8.8-22 (8-20)†
Raw Primary and Activated	18-24	50-80	>95	6.6-22 (6-20)
Digested Raw and Activated	18-24	50-70	>95	11-22 (10-20)
Pulp and Paper Wastes‡				
Box Board	22-33	86-94	-	-
Hard Board	26-28	85-95	-	-
White Water	21-30	78-94	-	-
Barker	32-40	90-93	-	-
Kraft	36-43	78-89	-	-
Specialty Paper	15	90	-	-
Softening Sludge	53-57	79-93	-	-

*Without chemicals.

†Cost of chemical conditioning to improve upon the 6%-10% cake.

‡For pump and paper sludges polymers could be used to increase capture to 95%-99% at a cost of \$3 to \$8 per ton.

TABLE E-35. CENTRIFUGE PERFORMANCE AND OPERATING COSTS FOR MUNICIPAL SLUDGE TREATMENT(2)*

	Plant A	Plant B	Plant C	Plant D
Plant Flow MLD (MGD)	68 (18)	19 (5)	10.2 (2.7)	30.2 (8.0)
Process	Primary Plus Trickling Filter with Anaerobic Digestion	Primary Treatment with Anaerobic Digestion	Primary Treatment Plus Activated with Anaerobic Digestion	Primary Plus Trickling Filter
Number of Units	One	One	One	Two
Machine Size, cm (in.)	61 x 96 (24 x 38)	61 x 96 (24 x 38)	61 x 152 (24 x 60)	61 x 96 (24 x 38)
Performance, Percent Solids				
Feed Solids	4-6	7.5-8.5	4.5-5	8
Cake Solids	18-24	30-35	20-25	30
Recovery	95-97	65-75	90-95	65-75
Chemical Used				
Dosage, \$/tonne (\$/ton)	3.3-6.6 (3-6)	-	8.8 (8)	-
Cost, \$/kg (\$/lb)	2.2 (2)	-	1.76 (1.60)	-
Operating Cost, \$/tonne (\$/ton)				
Maintenance	2.79 (2.53)	1.93 (1.75)	2.90 (2.63)	1.92 (1.74)
Operating Labor	2.98 (2.71)	1.04 (0.94)	7.91 (7.17)	1.10 (1.00)
Amortization†	1.43 (1.30)	14.55 (13.20)	14.1 (12.80)	3.56 (3.23)

*All costs based on 1973 dollars.

(Continued)

†Amortization based on 6% interest cost and amortized 25 years equals 7.823% of the capital cost as yearly cost.

TABLE E-35. Continued

	Plant A	Plant B	Plant C	Plant D
Operating Cost, $/tonne ($/ton) (Continued)				
Power	0.77 (0.70)	0.43 (0.39)	0.54 (0.49)	0.39 (0.35)
Chemicals	10.2 (9.30)	None	14.1 (12.80)	None
Total Cost	18.17 (16.54)	17.95 (16.28)	39.56 (30.74)	6.97 (6.32)
Ultimate Disposal	Landfill	Fertilizer/ Compost	Landfill/ Fertilizer	Incineration/ Landfill
Years of Service	4-5	7	5	13.2
Operating Schedule	24 hr/day	9 hr/week	21 hr/week	85 hr/week
Tonnes (Tons) Dry Sludge Solids Dewatered	54.9 (60.5)	7.8 (8.6)	14.3 (15.8)	31.8 (35.0)

*All costs based on 1973 dollars.

†Amortization based on 6% interest cost and amortized 25 years equals 7.823% of the capital cost as yearly cost.

4.0 Process Limitations(7)

- Scrolling of solids up the beach of the centrifuge must be carefully regulated by controlling the operating speeds, or high shearing forces caused by fluid drag from escaping liquid and by agitation of the scroll may carry solids back into the liquid pool.
- Relatively high maintenance requirements.
- Dewatered sludge is generated which requires disposal by incineration, landfill, or other method.

5.0 Process Economics - No capital cost data available; see Tables E-34 and E-35 for operating and chemical cost data.

6.0 Input Streams

6.1 Influent Wastewater/Sludge (Stream 1) - Sludge characteristics vary depending on the source. Will contain suspended and dissolved solids, oils, emulsions, heavy metals, etc.

7.0 Intermediate Streams

7.1 Liquids Discharge (Centrate) (Stream 2) - Will vary, depending upon composition of Stream 1. Will contain unreacted, excess coagulation chemicals.

8.0 Discharge Streams

8.1 Dewatered Solids (Stream 3) - See Tables E-34 and E-35.

9.0 Data Gaps and Limitations

Centrifugation has not been tested on sludges generated in coal gasification operations to determine optimum operating conditions.

10.0 Related Programs

None known.

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VACUUM FILTRATION

1.0 General Information

1.1 Operating Principle - Use of an applied vacuum to dewater a slurry or sludge by means of a rotary filter drum containing porous medium which retains the solid but allows the liquid to pass. Media used include cloth made of natural or synthetic filters, steel mesh, and tightly wound coil springs. Filter drum may be precoated with diatomaceous earth to facilitate breaking of emulsions, removal of suspended solids and traces of oil.

1.2 Development Status - Commercially available. Numerous units in operation throughout the world for municipal and industrial waste treatment, such as petroleum refinery sludges. Vacuum filtration is the most commonly used mechanical sludge dewatering method in the U.S.(1).

1.3 Licensor/Developer - Many vacuum filtration treatment systems and equipment are offered by numerous suppliers; a complete listing of these systems and their applications is available in the literature(2).

1.4 Commercial Applications - Numerous applications to municipal and industrial wastewaters. Commonly used in treatment of boiler treatment and blowdown and chemical or biological treatment sludges at petroleum refineries(3). Often used following treatment of sludges by coagulation-flocculation or emulsion-breaking techniques. No known applications to coal gasification wastes.

2.0 Process Information(4)

2.1 Flow Diagram - See Figure E-18.

- Process Description - Influent sludge (Stream 1) is fed to a sludge tank containing a rotating drum. As the drum passes through the sludge, solids are retained on the drum surface under an applied

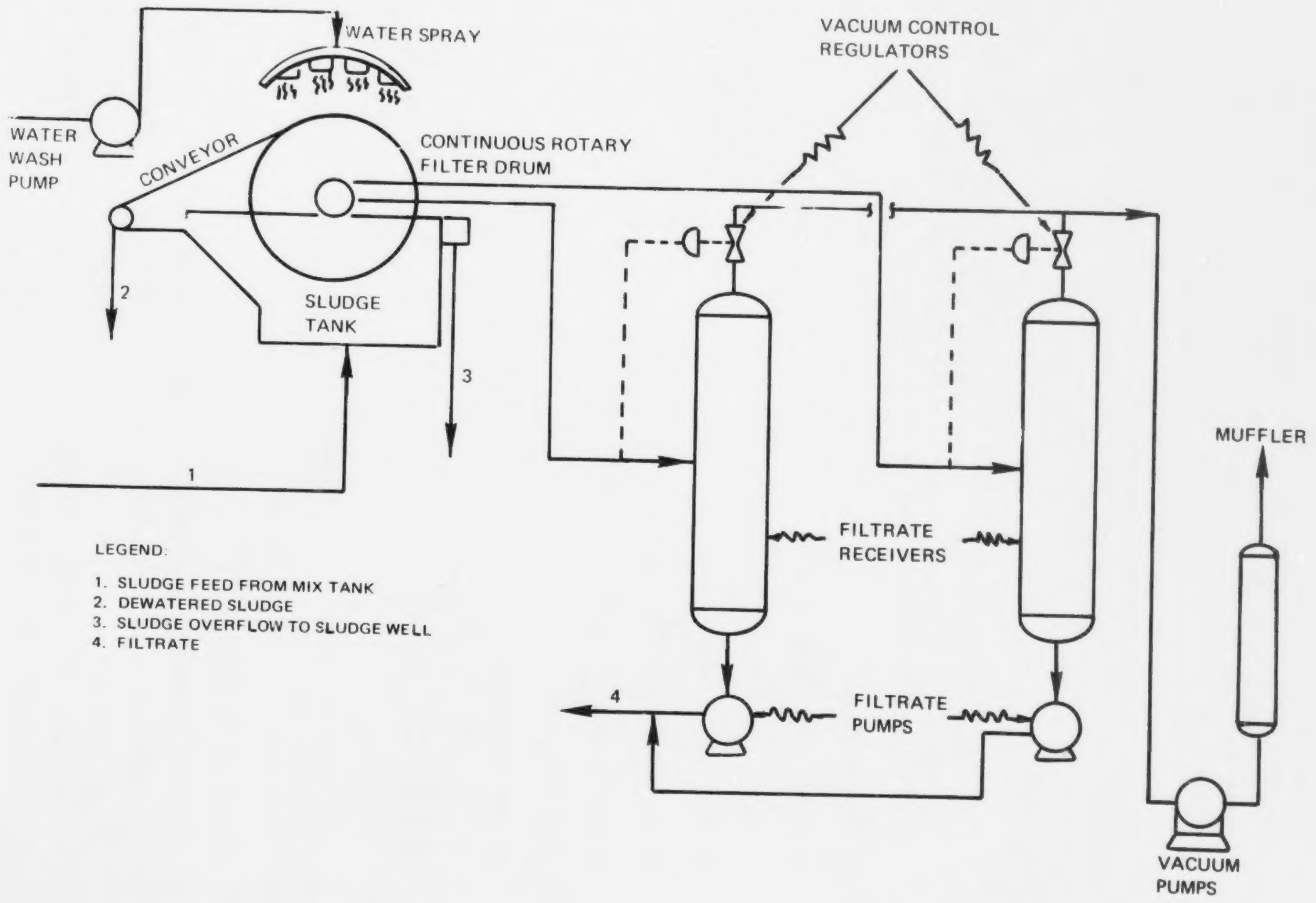
WATER SPRAY
VACUUM CONTROL REGULATORS
WATER WASH PUMP
CONVEYOR
CONTINUOUS ROTARY FILTER DRUM
2
SLUDGE TANK
3
1
LEGEND:
1. SLUDGE FEED FROM MIX TANK
2. DEWATERED SLUDGE
3. SLUDGE OVERFLOW TO SLUDGE WELL
4. FILTRATE
FILTRATE RECEIVERS
MUFFLER
4
FILTRATE PUMPS
VACUUM PUMPS

Figure E-18. Schematic of Vacuum Filtration Process vacuum; a cake of solids is built up, and filtrate (Stream 4) is removed by filtration through the deposited solids and the filter medium. As the drum emerges from the sludge tank, the deposited cake is further dried by liquid transfer to air drawn through the cake by the applied vacuum. At the end of the cycle, a knife edge scrapes the filter cake from the rotary filter drum to a conveyor for removal (Stream 2). Overflow sludge (Stream 3) is sent to a sludge well for recycle. The rotary filter drum is usually washed with water sprays at the end of a cycle before it is re-immersed in the sludge tank.

2.2 Equipment

- Filtration device (e.g., rotary drum, scroll-discharge, tilting-pan, disk, and batch leaf. Variations in the rotary drum include multicompartment, single compartment, belt, precoat, Corrco, hopper dewater, and top feed units.)
- Sludge tank.
- Water spray apparatus.
- Pumps (filtrate, vacuum, water-wash).
- Filtrate receivers.
- Vacuum control regulators.
- Miscellaneous equipment (pipes, mufflers, etc.).

2.3 Feed Stream Requirements(1)

- The dewaterability of sludges by vacuum filtration depends on factors such as the concentration, size, shape, and surface characteristics of the sludge particles, the extent of aggregation, the structural characteristics of the particles, and the viscosity, ionic strength and pH of the suspending water. Performance parameters which reflect the combined influence of these variables and which are calculated from measurable variables for determination of optimum operating conditions for a given vacuum filtration system are the specific resistance ($\overline{\varsigma}$) and the coefficient of compressibility ($\mathring{s}$) of the waste.

2.4 Operating Parameters(5,6)

Operating parameters and design consideration include: sludge feed concentration, sludge viscosity, filtrate viscosity, operating vacuum, type and porosity of filter media, degree of sludge thickening preceding filtration, thickening chemical, drum submergence time, and drum speed. See Table E-36.

TABLE E-36. TYPICAL SEWAGE SLUDGE FILTRATION CHARACTERISTICS AND RATES(7)

Sludge Type	Feed Solids, %	Filtration Rate, Dry kg/hr-m^3 (Dry lbs/hr-ft^2)	Average Cake Moisture	Chemicals	
				$FeCl_3$	CaO
Primary Sludge					
Raw	8	48.9 (10.0)	66	1.5	7.0
Digested	8	39.1 (8.0)	70	3.0	8.5
Digested - Elutriated	8	31.8 (6.5)	71	2.5	4.0
Primary - Trickling Filter					
Raw	7	43.9 (9.0)	68	1.5	8.0
Digested	8	34.2 (7.0)	71	3.0	8.5
Digested - Elutriated	8	31.8 (6 5)	72	2.5	4.0
Primary - Activated Sludge					
Raw	5	21.9 (4.5)	79	4.0	4.0
Digested	6	21.9 (4.5)	76	4.0	9.0
Digested - Elutriated	6	21.9 (4.5)	78	5.0	5.0
Activated Sludge - Concentrated	3	9.8 (2.0)	84	-	0

2.5 Process Efficiency and Reliability - See Table E-37.

Vacuum filtration techniques are widely used and proven highly reliable for dewatering a range of sludge wastes.

2.6 Raw Materials Requirements

- Sludge Conditioning Chemicals - Chemicals such as $FeCl_3$ and lime reduce the specific resistance of sludge and increase their filtration rate. See Tables E-36 and E-37 and data sheet on coagulation-flocculation.
- Diatomaceous Earth - Filtration media for precoat vacuum filtration.
- Water - For water spray used to wash filtration apparatus.

2.7 Utility Requirements

- Electricity - Used for driving pumps and for central drive unit on filtration apparatus. Requirements vary with the specific design and removal efficiency desired.

TABLE E-37. TYPICAL VACUUM FILTRATION RESULTS(5)

Sludge Type	Thickened Solids, Weight Percent	Chemical Requirements, Wt. %		Filter Yield, kg/hr-m^2 (lb/hr-ft^2)	Cake Moisture, Wt. %
		$FeCl_3$	CaO		
Raw	6-10	1-2	5-7	24.4-34.2 (5-7)	65-70
Digested	6-10	1-4	6-10	29.3-39.1 (6-8)	70-75
Raw + Trickling Filter	5-7	2-4	8-12	29.3-39.1 (6-8)	75-80
Raw + Activated Sludge	4-6	2-4	8-12	14.7-24.4 (3-5)	75-80
Activated Sludge	2-4	8-10	-	2.4-9.8 (0.5-2)	80-85

3.0 Process Advantages(1,5)

- Widely used commercial process for which extensive operating experience is available.
- Minimal raw materials requirements.
- Suitable for treatment of a wide variety of sludges with differing physical and chemical properties.

4.0 Process Limitation(5,8)

- Dewatered sludge is generated which requires disposal by incineration, landfill, or other methods. For precoat vacuum filtration, spent diatomaceous earth is generated which also requires ultimate disposal.
- Evaluation and operating conditions of vacuum filters on specific sludges require determination by laboratory "leaf" tests.
- Continuous pilot-scale tests may be required when design information for large vacuum filtration installation is needed.
- Certain vacuum filtration systems, especially precoat vacuum filtration systems, have large capital investment and high operating costs.

5.0 Process Economics - See Tables E-38 and E-39.

6.0 Input Streams

6.1 Sludge Feed From Mix Tank (Stream 1) - Sludge characteristics vary depending on the source. May contain dissolved and suspended solids, oils, emulsions, heavy metals, etc.

7.0 Intermediate Streams

None.

8.0 Discharge Streams

8.1 Dewatered Sludge (Stream 2) - Moisture content of dewatered sludge is typically between 60%-80% (see Tables E-36 and E-37). Other characteristics will vary depending on those of Stream 1.

8.2 Sludge Overflow to Sludge Well (Stream 3) - Same as Stream 1.

8.3 Filtrate (Stream 4) - Will vary, depending upon composition of Stream 1. Will contain unreacted, excess coagulation chemicals.

TABLE E-38. VACUUM FILTRATION COSTS OF PRIMARY ACTIVATED DIGESTED SLUDGE(7)* IN 1973 DOLLARS

Parameter	Cost, $/Tonne ($/Ton) Dry Solids	Percent of Total Operating Cost
Chemicals	6.37 (5.79)	49
Direct Labor	2.57 (2.34)	20
Supervision and Maintenance Labor	2.57 (2.34)	20
Power	1.2 (1.09)	9
Supplies	0.25 (0.23)	2
Total Operating Cost	12.97 (11.79)	100
Amortization and Interest	2.00 (1.82)	
Grand Total	14.97 (13.61)	

*For municipal treatment system handling 12,400 tonnes (13,700 tons) solids/year, using 4.8 m (16 ft) diameter rotary vacuum filter.

TABLE E-39. COSTS FOR SLUDGE THICKENING AND VACUUM FILTRATION OF PETROLEUM REFINERY SLUDGES (1967 DOLLARS)(3)

	Small Refinery*		Medium Refinery†		Large Refinery‡	
	Capital Costs	Annual O&M Costs	Capital Costs	Annual O&M Costs	Capital Costs	Annual O&M Costs
Older Technology	120,500	22,000	150,000	50,000	265,000	58,750
Typical Technology	59,000	11,500	82,500	20,500	108,500	22,500
Newer Technology	35,000	9,500	62,500	12,000	82,500	20,500

*Up to 4.2×10^6 liters (35,000 bbl) per day capacity.

†4.2×10^6 to 1.2×10^7 liters (35,000-100,000 bbl) per day capacity.

‡Greater than 1.2×10^7 liters (100,000 bbl) per day capacity.

9.0 Data Gaps and Limitations

Vacuum filtration has not been tested on sludges generated in coal gasification operations to determine the most suitable operating conditions.

10.0 Related Programs

None known.

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DRYING BEDS

1.0 General Information

1.1 Operating Principle - Dewatering of a sludge by application to beds consisting of a top layer of sand and a bottom layer of gravel underlain by drainage laterals leading to sumps. Initial water loss is due primarily to filtration of the water through the sludge and percolation into the sand; after several days, water loss is due mainly to evaporation.

1.2 Development Status - In use on a commercial scale. Drying beds are used for dewatering principal and industrial sludges(1).

1.3 Licensor/Developer - Sludge drying bed treatment systems and construction materials are offered by numerous design firms and suppliers. Sources are available in the literature.

1.4 Commercial Applications - Method is in widespread use in municipal wastewater treatment systems. In use at SASOL Lurgi-type coal gasification facility in Sasolburg, S. Africa(2). Also in use in numerous industrial facilities, including petroleum refineries.

2.0 Process Information

2.1 Flow Diagram - See Figure E-19

- Process Description - Sludge to be dried (Stream 1) is applied to the surface layer of sand in the drying bed. The bed is surrounded by low walls to retain the sludge and to segregate the beds from neighboring beds. Water from the sludge percolates through the sand and gravel layers of the bed and drains through open-jointed tiles to underground laterals, then is conveyed to sumps for removal (Stream 2). Dried sludge (Stream 3) is periodically removed, usually by manual methods, and the bed is returned to service.

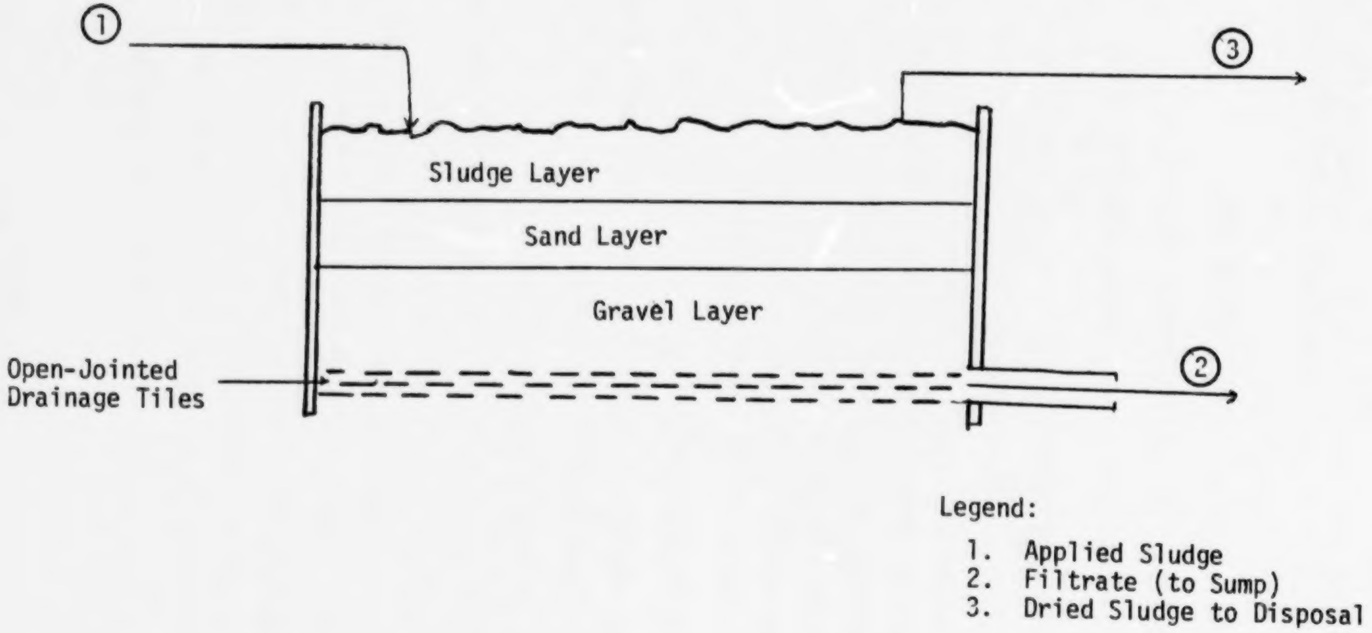
①
③
Sludge Layer
Sand Layer
Gravel Layer
Open-Jointed Drainage Tiles
②
Legend:
1. Applied Sludge
2. Filtrate (to Sump)
3. Dried Sludge to Disposal

Figure E-19. Schematic of Sludge Drying Bed

2.2 Equipment[1,3]

- Drying bed consisting of 10-22.5 cm (4-9 in.) of sand over 20-45 cm (8-18 in.) of graded gravel over open-jointed tiles for drainage.
- Retainer walls to enclose drying bed.
- Lateral drainage system, sumps, etc.
- Bed cover material (e.g., glass, plastic, etc.)

2.3 Feed Stream Requirements[3]

Organic sludges should be pretreated (e.g., by digestion, congulation flocculation, etc.) prior to application to enhance drainability and to prevent the formation of undesirable odors. The dewaterability of the sludge is a function of its concentration, size, surface characteristics, extent of aggregation and other structural characteristics, as well as the quantity, viscosity, ionic strength and pH of the suspending water.

2.4 Operating Parameters[4]

Principal operating parameters are sludge loading (wt/unit area and depth of application), and length of stay. See Table E-40.

2.5 Process Efficiency and Reliability[5]

Efficiency depends on the type and design of the system used, on the nature of the sludge treated, and the duration of its residence time in the bed. Typically, the applied sludge allowed to dry 10-15 days to achieve approximately 60% moisture content.

2.6 Raw Materials Requirements - None specific to the process. However, sludge conditioning chemicals may be required to enhance sludge dewaterability (e.g., alum, ferric chloride, etc.).

2.7 Utility Requirements - None (except for pumping)

TABLE E-40. SLUDGE DRYING BED DESIGN DATA[4]

Sludge	Sludge Loading kg dry solid/m^2-yr (lb dry solids/ft^2-yr)
Primary	97.8-146.6 (20-30)
Primary + Trickling Filter	97.8-146.6 (20-30)
Primary + Activated Sludge	48.9-73.3 (10-15)

3.0 Process Advantages[1,4]

- Minimal raw materials requirements.
- Simple to operate.
- Suitable for treatment of a wide variety of sludges with differing physical and chemical properties.
- Costs are usually low.

4.0 Process Limitations[1,4]

- Significant amounts of labor are required to lift and remove dried sludge from the beds.
- Large land area required.
- Efficiency of drying is dependent upon climatic conditions.
- Dewatered sludge is generated which requires disposal by incineration, landfill, or other methods.
- Can cause an odor problem.

5.0 Process Economics

No actual data available. Costs depend on land value; sludge volume; equipment and labor for dry sludge removal.

6.0 Input Streams

6.1 Applied Sludge (Stream 1) - Sludge characteristics will vary, depending on the source. May contain dissolved and suspended solids, oils, emulsions, heavy metals, etc.

7.0 Intermediate Streams

None.

8.0 Discharge Streams

8.1 Filtrate (to sump) (Stream 2) - Will vary, depending on composition of Stream 1. May contain excess sludge conditioning chemicals.

8.2 Dried Sludge to Disposal (Stream 3) - Moisture content of sludge dried 10-15 days is approximately 60 percent. Other characteristics will vary, depending on composition of Stream 1.

9.0 Data Gaps and Limitations(3,6)

In the past, bed requirements have been based only on empirical relationships or experience factors. Investigators have recently attempted to derive design criteria from laboratory experiments and pilot operations. Although several selected variables on sludge drying have been studied in the laboratory and in pilot-scale operations, further studies are needed to develop engineering criteria for the design of full-scale systems.

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EMULSION BREAKING

1.0 General Information

1.1 Operating Principle - Coalescence and separation of the oil and water phases in a wastewater emulsion by physical methods (e.g., heating, distillation, centrifuging, precoat vacuum filtration and electrolytic methods) and by chemical methods.*

1.2 Developmental Status - Commercially available.

1.3 Licensor/Developer - Equipment and chemicals for emulsion breaking processes are offered by numerous suppliers. Some licensed or patented versions of physical emulsion breaking processes are the Oliver precoat vacuum filter and the Cottrell electrical precipitator. Japan's Mitsubishi Petrochemical Company has developed and is currently operating an electrolytic coagulation system using iron anodes(2). A listing of other manufacturers is presented in technical and trade journals (e.g., Ref. 1). Chemical agents for emulsion breaking are available through chemical supply firms.

1.4 Commercial Applications - Many applications to petroleum refinery effluents, including recovered oil from API separators and other oily emulsions. No known applications to coal gasification.

2.0 Process Information

2.1 Flow Diagram - Figure E-20 depicts emulsion breaking by chemical treatment combined with precoat vacuum filtration and heating. Influent oil emulsion (Stream 1) is heated in a heat exchanger and discharged into a settling tank maintained at 338°K-350°K (150°F-170°F).

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*See draft data sheet on centrifugration and vacuum filtration for additional data in these processes.

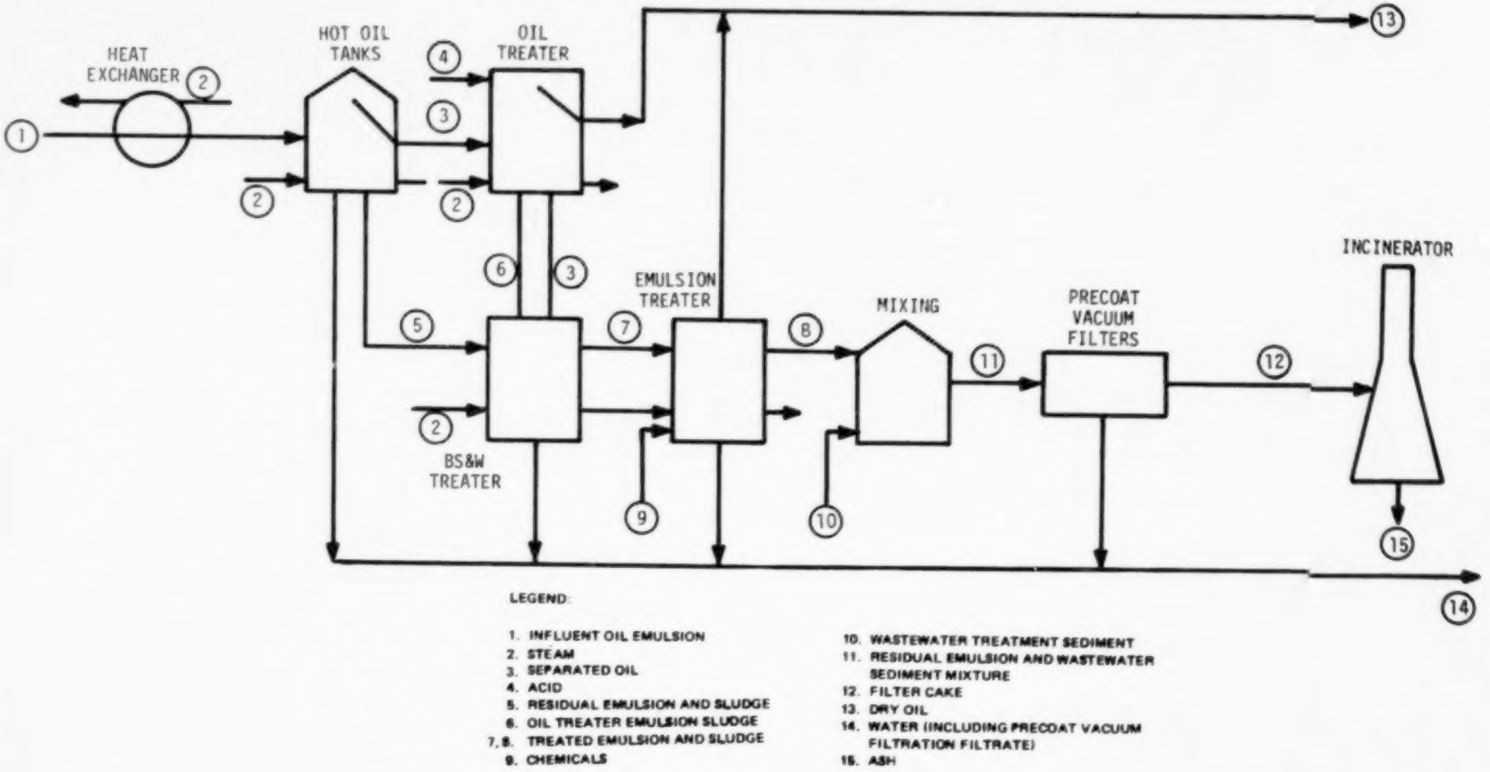
HEAT EXCHANGER
HOT OIL TANKS
OIL TREATER
EMULSION TREATER
BS&W TREATER
MIXING
PRECOAT VACUUM FILTERS
INCINERATOR
①
②
③
④
⑤
⑥
⑦
⑧
⑨
⑩
⑪
⑫
⑬
⑭
⑮
LEGEND:
1. INFLUENT OIL EMULSION
2. STEAM
3. SEPARATED OIL
4. ACID
5. RESIDUAL EMULSION AND SLUDGE
6. OIL TREATER EMULSION SLUDGE
7, 8. TREATED EMULSION AND SLUDGE
9. CHEMICALS
10. WASTEWATER TREATMENT SEDIMENT
11. RESIDUAL EMULSION AND WASTEWATER SEDIMENT MIXTURE
12. FILTER CAKE
13. DRY OIL
14. WATER (INCLUDING PRECOAT VACUUM FILTRATION FILTRATE)
15. ASH

Figure E-20. Treatment of Recovered Oil by Chemical Demulsification and Precoat Vacuum Filtration

After about 24 hours, the separated oil layer (Stream 3) is pumped to an oil treater, where the oil is heated to 355°K-365°K (180°F-200°F) and acid (Stream 4) is added to assist in emulsion breaking. After about 48 hours, the oil is skimmed off (Stream 13) and pumped to the refinery for reprocessing. The residual emulsion and sludge (Stream 5) are pumped to a bottom sediment and water (BS&W) treater, where they are heated by steam coils, then pumped (Stream 7) to an emulsion treater tank for chemical treatment; separated water (Stream 14) is removed. After two weeks, the oil separated in the emulsion treater (Stream 8) and the separated water are removed. Unbroken emulsions and sludge are pumped to a mixing tank where other plant sludges (Stream 10) are added. The mixture (Stream 11) is then fed to continuous rotary vacuum precoat filters. The filtrate is combined with the separated water and sent to plant oil/water separators and the filter cake (Stream 12) is fed to an incinerator.

In electrolytic coagulation processes, the influent emulsion is passed through a tank containing two electrodes. A high potential pulsating electrical current is applied, which causes the water globules in the emulsion to coalesce. When the masses attain a certain weight, they settle by gravity and are withdrawn.

The distillation process of emulsion breaking involves the use of heat to weaken the interfacial films of emulsions and permit coalescence and separation of the oil and water phases. Waste emulsions enter the distillation column, where water and light ends of the oil are vaporized, then are condensed and withdrawn as liquid. Residual oil remains in the bottom of the apparatus and is removed for recycle or disposal.

2.2 Equipment - Depending on the process used, equipment may include: rotary vacuum precoat filters, centrifuge apparatus, heat exchangers, pumps, distillation column or tower, electrical precipitator apparatus (e.g., metal electrodes) or chemical treater unit.

2.3 Feed Stream Requirements

- Loading - varies with the specific emulsion treatment system, removal efficiencies desired, and specific design.
- pH - proper pH facilitates breaking of certain emulsions. Adjustment of pH to optimum value may be accomplished by addition of caustic or acid.

2.4 Operating Parameters(3) - Flow rates, temperatures, and retention times vary with the specific process used and the waste treated. Retention times of two weeks or longer in chemical demulsification units are typical for API separator emulsions in petroleum refineries. Temperatures of 338°K-365°K (15°F-200°F) are used in heating emulsions both with and without simultaneous chemical treatment. See Table E-41 for operating parameters for precoat vacuum filtration.

2.5 Process Efficiency and Reliability - Efficiency depends upon the type and design of the method used, and on the nature of the emulsion. Emulsions consist of mixtures of water and oil phases and a third phase known as the stabilizing interfacial film which binds the oil and water phases together and must be removed or destroyed for effective emulsion breaking. Emulsions may be ionic, non-ionic, colloidal (hydropholic or hydrophilic), or may consist of solid particles which are surface active. It is essential that the chemical or physical method used for emulsion breaking suit the characteristics of the specific emulsion being treated; laboratory-scale testing of an emulsion is sometimes required in order to identify the appropriate method. Emulsion breaking processes have been widely used and proven highly reliable for treatment of a range of industrial emulsions.

2.6 Raw Materials Requirements

- Emulsion breaking chemicals - include acids (sulfuric acid), caustics (sodium hydroxide, lime), salts (iron sulfate, calcium chloride, sodium silicate, sodium sulfate, alum), and commercial organic treatment chemicals.
- Diatomaceous earth - filtration media for precoat vacuum filtration.

TABLE E-41. OPERATING DATA FOR PRECOAT VACUUM FILTRATION OF API SEPARATOR EMULSIONS(4)

Parameters	Value
Waste Characteristics:	
Specific Gravity	1.0-1.08
Solids, % by Weight	2.1-79
Water, % by Weight	2.4-85
Oil, % by Weight	0.29-20
Kg/MM l (lb/MM Gal) Sludge/Flow	110-1285 (64-748)
Volumetric Filtration Rate, $l/m^2 \cdot hr$ ($gal/ft^2 \cdot hr$)	24.4-58.9 (0.6-1.45)
Solids Removed by Filtration, kg/m^2 hr ($lb/ft^2 \cdot hr$)	1.14-1.58 (0.233-0.323)
Sludge Cake Characteristics:	
Percent Water	21
Percent Oil	24
Fuel Value, kcal/lb (Btu/lb)	5800 (10,500)

2.7 Utility Requirements

- Steam - used for facilitating coalescence and separation of emulsion phases. Quantity used depends on waste being treated and loading.
- Electricity - used for emulsion breaking by application of strong electric fields in which the waste is passed between two electrodes and subjected to a high-potential pulsating current. Also used for driving centrifuges, pumps, compressors, etc. Requirements vary with the specific process design and efficiency desired.

3.0 Process Advantages(3,4)

- Effective for separation and recovery of oil from emulsions produced in API separators or other pollution control processes.
- Suitable for treatment of a wide variety of waste emulsions with differing physical and chemical properties.
- Little or no raw materials requirements for some methods (e.g., distillation, centrifugation, heating).

4.0 Process Limitations(3,4)

- Emulsion breaking technology is only quasi-scientific and trial-and-error experimentation and lab-scale testing are required to determine the specific process and the proper operating conditions to be implemented.
- Unresolved emulsions and sludge are generated requiring disposal, often by incineration with landfill of residual ash.
- Certain processes (e.g., distillation, precoat vacuum filtration) generate residuals which require subsequent disposal.

5.0 Process Economics

No data available. Centrifugation and precoat vacuum filtration have greater operating and capital investment costs compared to other emulsion breaking processes.

6.0 Input Streams

6.1 Influent Oil Emulsion (Stream 1) - Characteristics will vary depending on the waste source. See Table E-41 for petroleum refinery API separator emulsion characteristics.

6.2 Steam (Stream 2) - See Section 2.7.

6.3 Acid (Stream 4) - Used to assist in emulsion breaking in conjunction with heating. See Section 2.6.

6.4 Chemicals (Stream 9) - See Section 2.6.

6.5 Other Plant Sludges (Stream 10) - Characteristics will vary depending on the waste source.

7.0 Intermediate Streams

7.1 Separated Oil (Stream 3) - No data available on characteristics; will be similar to dry oil (Stream 7).

7.2 Residual Emulsion and Sludge (Stream 5) - No actual data available on characteristics. Will contain oil, water, dissolved and suspended matter.

7.3 Oil-Treater Emulsion Sludge (Stream 6) - Consists of oil sludge, residual dissolved and suspended matter, and residual acid from the oil treater operations. No composition data available.

7.4 Treated Emulsion and Sludge (Streams 7 and 8) - No composition data available. Similar to dewatered Streams 5 and 6, plus residual treatment chemicals (Stream 8).

7.5 Residual Emulsion and Wastewater Sediment Mixture (Stream 11) - Combination of Streams 5 and 9.

8.0 Discharge Streams

8.1 Separated Oil (Stream 13) - Consists of separated oil from treater units. Composition will vary, depending on waste source. May contain residual acid and chemicals from treatment operations.

8.2 Filter Cake (Stream 12) - Consists of suspended solid material, diatomaceous earth, precoat filter chemicals, and occluded emulsion treatment chemicals. Cake can usually be burned with the production of heat in excess of that required to sustain combustion. See Table E-41.

8.3 Water (Including Precoat Vacuum Filtration Filtrate) (Stream 14) - Consists of wastewater separated from the influent emulsion in the BS&W and emulsion treater units, and filtrate from precoat vacuum filtration. Constituents will vary, depending on the waste and treatment chemicals used.

8.4 Ash (Stream 15) - Produced by incineration of filter cake(Stream 12). Suitable for land disposal.

9.0 Data Gaps and Limitations

Emulsion breaking processes have not been tested on emulsions produced in coal conversion operations.

10.0 Related Programs

None known.

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APPENDIX F

SOLID WASTE MANAGEMENT

Incineration
Land Disposal
Chemical Fixation/Encapsulation

INCINERATION

1.0 General Information

1.1 Operating Principle - Controlled combustion of waste to destroy organics and decrease waste volume. Incineration results in the formation of carbon dioxide, water, ash and other inorganic compounds.

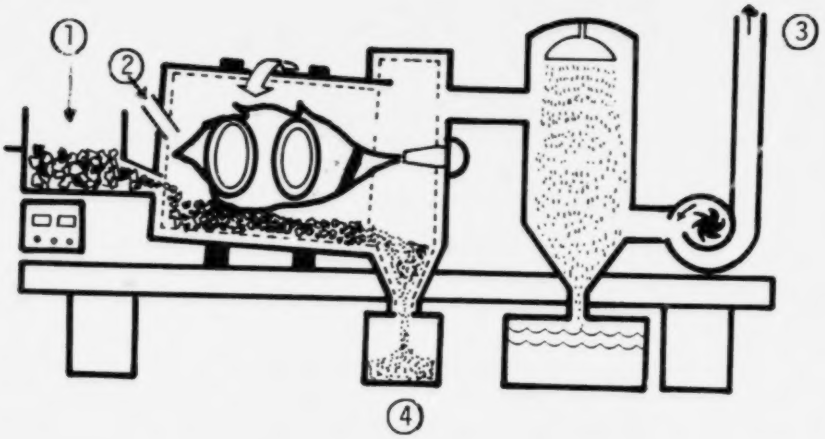
1.2 Development Status - Commercially available; numerous units in worldwide operation for disposal of municipal and industrial solid wastes and sludges.

1.3 Licensor/Developer - Numerous incinerator systems and equipment are available through various suppliers. These include: 1) the Dorr-Oliver fluidized bed incinerator; 2) the Bartlett-Snow rotary kiln incinerator; and 3) multiple hearth incinerator systems. Complete listings of these systems and their suppliers are presented in the literature(1).

1.4 Commercial Applications(2,3) - Applications include: a) refinery wastes, such as spent caustic solutions, API separator bottoms, DAF float, waste biosludge and slop oil emulsion solids; b) municipal sewage sludges; c) industrial waste activated sludges; d) neutral sulfite semi-chemical paper mill waste liquors; and e) pharmaceutical wastes. No known application to coal gasification wastes.

2.0 Process Information(4)

2.1 Flow Diagram (See Figure F-1) - Most incineration systems consist of four basic components: a) a waste storage facility; b) a burner and oxidation chamber, where the influent waste (Stream 1) is combusted in the presence of air or oxygen (Stream 2) and secondary pollutants (CO, CO_2, NO_x, SO_x and halogen-containing compounds) are formed;



Legend:

1. Influent Waste
2. Air
3. Flue Gas
4. Residuals

Figure 1. Portable Rotary Kiln Incineration Unit

c) an effluent purification system, when warranted; d) a vent or stack, for discharge of combustion gases (Stream 3); and e) an ash removal mechanism (Stream 4).

2.2 Equipment

- Incinerator - Varies with the type of waste incinerated. Three types of incinerators (i.e., fluidized bed, rotary kiln and multiple hearth) are commonly used in solids and sludge combustion; multiple chamber and retort incinerators are also used for the incineration of solids. Are constructed of refractory materials suited to the desired operating temperature of the incinerator. See Table F-1 for design parameters.
- Oxidant Source Equipment - For supply of air. Required equipment may include blowers, pumps, plenums, etc.
- Bed material, such as sand (for fluidized bed combustors).
- Auxiliary Burners (oil or gas-fired)

2.3 Feed Stream Requirements

- Combustibility - Waste must contain sufficient carbonaceous matter to be combustible. Depending on the water content, combustion of biosludges and other wastes produced during gasification of coal may require supplemental fuel.
- Calorific Value - Adequate heat balance (e.g., the difference between heat evolved from combustion and heat absorbed due to vaporization, radiation, etc.).
- Moisture Content - Excessive moisture must be removed from slurried wastes to minimize the amount of auxiliary fuel required; moisture content less than 60% typically required.
- Corrosiveness - The corrosiveness of the waste must be accommodated. by the materials of construction of the incinerator chamber.
- Sulfur, Halogen, and Inorganic Ash Content - Wastes containing these constituents from combustion products (e.g., SO_x, halogen acids, and inorganic oxides) which may require removal by pollution control equipment, such as wet scrubbers, electrostatic precipitators and fabric filters.

2.4 Operating Parameters - See Table F-1 - Feed rates depend on feed characteristics and the furnace design. Feed rates for multiple hearth incinerators vary from 35-60 $kg/hr/m^2$ (7-12 $lb/hr/ft^2$)$^{(5)}$.

TABLE F-1. TYPICAL DESIGN AND OPERATING PARAMETERS FOR FOUR TYPES OF INCINERATOR UNITS(4)

Parameter	Incinerator Type			
	Rotary Kiln*	Multiple Hearth*	Fluidized Bed*	Multiple Chamber†
Dimensions	Length/Diameter Kiln Ratio of 1:5	(7.9 - 279 m^2) 85-3000 ft^2 Hearth Area Overall Height: 4.75 - 16.6 m (15 ft 7 in. - 54 ft 7 in.)	Bed Diameter <15.3 m (<50 ft)	Length/Width Ratio of Retort: 2:1
Residence Time	Seconds to Hours	Seconds to Hours	Seconds to Hours	Seconds to Hours
Temperature	1144-1922°K (1600-3,000°F)	Combustion Zone: 1033-1255°K (1400-1800°F) Upper Hearth: 589-801°K (600-1000°F) Cooling Hearth: 513-589°K (400-600°F)	760-871°C (1400-1600°F)	811°K (1000°F)
Air Requirement	—	—	1.5-2.1 m/sec (5-7 ft/sec)	300% excess air
Capacity	37.3-746 kg/hr (100-2000 lb/hr)	(22.9-39.4 kg/m^3-hr) 7-12 lb/ft^2-hr	—	280-373 kg/hr (750-1,000 lb/hr)

*Suitable for sludge and solids incineration.

†Suitable for solids incineration.

2.5 Process Efficiency and Reliability - Efficiency depends upon the type wastes incinerated, and temperature and residence time in the combustion chamber. Incineration of waste solids and sludges is widely performed and has been proven reliable. Occasional operational difficulties may arise due to the type of waste incinerated; e.g., the incineration of sludge containing chlorides and alkali elements at low temperatures may lead to plugging in the exhaust gas ducts by ash deposits(2).

2.6 Raw Material Requirements

- Fuel - For incineration of sludges having inadequate heat value, and for start-up; for a waste sludge with a moisture content of 95 percent and a dry heating value of 5500 kcal/kg (10,000 Btu/lb), 3.1 Nm^3/tonne (100 scf/ton) of natural gas is required(4).
- Air - Required to support combustion. See Table F-1.
- Water - May be required for pollution control equipment (e.g., scrubbers); requirements depend on specific system used and emission restrictions.

2.7 Utility Requirements

- Electricity and Water - May be required for pollution control equipment; requirements vary with system used.

3.0 Process Advantages(6)

- Suitable for disposal of many types of wastes, including organic and partially inorganic sludges and solids, including biosludges.
- Reduces sludges and solids to inert, sterile gases and residuals; also eliminates waste odors.
- Widely used method for which extensive commercial-scale operating experience on sludges and solid is available.
- Minimal raw materials requirements (except for auxiliary fuel, when required).

4.0 Process Limitations

- Generates residual solids (ash) requiring disposal.
- Can generate air pollutants such as particulates, sulfur dioxide, nitrogen oxides, and metals such as mercury, as well as hydrocarbons and carbon monoxide.

- To minimize air pollutant discharges, expensive pollution control equipment may be required.

- Process has high capital and operating costs.

5.0 Process Economics

Capital investment costs will vary depending on the type of incinerator, the type and quantity of waste being incinerated, and the nature of pollution control equipment. Operating costs are a function of the amount of secondary fuel required, the replacement of refractory linings, and labor.

6.0 Input Streams (See Figure F-1)

6.1 Influent Waste (Stream No. 1) - Will vary depending on the source. Coal gasification wastes such as chars, tars/oily sludges and biosludges are candidate wastes.

6.2 Air (Stream No. 2) - See Section 2.6.

7.0 Discharge Streams

7.1 Flue Gas (Stream No. 3) - Consists primarily of CO_2, water, and air. Also contains particulates which vary in quantity and size depending on the type of waste incinerated, operating procedures, and completeness of combustion. May also contain hydrocarbons and CO due to incomplete combustion. Sulfur dioxide, nitrogen oxides, and metals such as Hg may also be components of the flue gas.

7.2 Residuals (Stream No. 4) - Consist of inorganic, noncombustible materials including ash and other materials present in the influent waste (e.g., iron/steel, glass ceramics in municipal wastes). Require ultimate disposal in landfills or by other suitable methods.

8.0 Data Gaps and Limitations

- Limited data are available on the fate of high molecular weight organics in tars/oils in incinerators. Materials not destroyed by incineration may remain as vapors in the flue gas or may be associated with the ash.

- The combustibility of chars and tars/oily sludges from coal gasification has not been studied/established.

9.0 Related Programs

None known.

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LAND DISPOSAL PROCESS

(Landfilling, Land Burial, and Application to Soils)

Four major methods of land disposal of coal gasification waste solids and sludges are: (a) return of the wastes to deep mines; (b) return to surface mines; (c) conventional landfilling techniques; and (d) soil application. Key features of these methods are presented below.

A. Return to Deep Mines(1,2)

Involves return of solid wastes/sludges directly to an underground mine for ultimate disposal. The applicability of the method would be a function of the haul distance to the mine, as well as the physical and hydrogeological conditions of the mine.

Applicability: All types of solid wastes from coal gasification (including ash, tars, and oily sludges, and biosludges) could be disposed of in deep mines. The more hazardous wastes, such as heavy metal catalysts, should be containerized prior to deposition in the mine to minimize environmental contamination.

Development Status: The procedure of waste return to deep mines is an untried method which as not yet been field tested. However, procedures for this type of disposal are currently being developed for the oil shale industry for the Bureau of Mines(1).

Operating Considerations/Disadvantages:

- Time Delay - Wastes could not be returned to the mine until sufficient space became available so that the disposal operation would not interfere with the mining operation.
- Technology Modification - Return of the wastes to an underground mine would require extensive changes in mine operation procedures which were originally designed to remove rather than insert large quantities of material. Underground backfilling would require design and use of permanent haulways and access routes for trucks and/or conveyors.

- Potential for groundwater contamination - Returning coal gasification wastes underground carries the potential for groundwater contamination if water which percolated into the backfilled areas or water contained in the waste sludge were to leach the wastes and exit the mine area. Contaminants which could be mobilized would depend on the nature of the waste, but could include soluble salts and organics and suspended solids. These contaminants could eventually reach surface waters. The most suitable mines for disposal would be those whose geological and hydrological characters would minimize the potential for groundwater contamination.

- Compaction - Compaction would: (a) maximize the volume of the waste that would be returned to the mines; (b) minimize leaching of soluble inorganics/organics and suspended solids. Solids may have to be compacted to reduce volume prior to deposition in mines. When in place, compacted wastes may help control surface subsidence of the mine. Compaction could be accomplished either above ground or within the mine. The operation of heavy mechanical compaction equipment below ground would require special operating techniques and considerable void space to accommodate equipment maneuvering. Special safety precautions would also be needed to minimize the hazards to personnel associated with equipment moving and working in close quarters.

- Haulage Requirements - Waste can be returned to the mine by means of short-haul trucks or pumped into the mine as a slurry. Drainage pipes or pumps would be needed to collect and control the excess water used in the slurrying operation. The slurry method would have a greater potential for groundwater contamination due to possible leaching of the waste and migration of the slurry water.

- Transportation Costs - Costs would be very high, if the gasification plant is located at a significant distance from the mine.

Advantages:

- Suitable for many types of wastes, if adequate provisions for environmental protection are employed.

- Method is flexible; wide variations in waste loads are readily accommodated.

- Does not require the availability of large tracts of surface land, as in landfilling.

- Waste is sheltered from many natural forces of erosion, such as wind and precipitation.

- Method requires no revegetation or other surface stabilization procedures.

- Can be beneficial from the standpoint of reducing surface subsidence.

Costs:

Costs associated with return of wastes to deep mines would be functions of:

- -- The amount of waste returned to the mine; the more waste that could be disposed of below ground, the less that would require costly surface disposal.
- -- Equipment and labor; the use of haul trucks, pneumatic conveyors and compaction equipment would be significant operating costs associated with disposal
- -- Mine modification; the return of processed solids and other wastes to the mine may require extensive modification of the mine work area, ventilation systems, etc.

B. Return to Surface Mines(2)

As with deep mines, surface mines are likely to be available near coal gasification facilities and may be suitable and economical for use in waste disposal, depending on the distance of the mine from the site and on the environmental suitability of the site.

Applicability: Same as for return to deep mines - see Section A.

Development Status: Although coal gasification wastes have not been disposed of using this method, the method has been used for the disposal of municipal refuse, sewage sludges, and power plant fly ash. Reclamation of surface coal mines using earthen fill has been suspended at several sites.

Operating Consideration/Disadvantages:

- Time Delay - Wastes cannot be returned to the mine until sufficient room is available so that the disposal operation does not interfere with mining operations.
- Erosion Control - Erosion control measures would be required to minimize exposure of the wastes to wind, rain, snow, and other natural forces. Once filled, the waste disposal area of the mine could be levelled by bulldozers and covered with topsoil and/or other suitable materials and vegetated for further erosion control and to improve the appearance of the site. Interim stabilization techniques may be implemented, such as application of straw or mulch to cover the deposited waste.

- Compaction - Compaction of the waste would increase mine capacity to receive waste and would further reduce the erosion potential due to wind and water action. Compaction could be accomplished more easily at a surface rather than a deep mine, since special below ground operating techniques and safety precautions would not be required.
- Haulage Requirement - Same as for return to deep mines.

Advantages:

- No additional acreage required for disposal.
- Suitable for disposal of many types of wastes, if adequate provisions for environmental protection are employed.
- Method is flexible; wide variations in waste loads are readily accommodated.
- Less complicated and hazardous than return to deep mines.
- Technology for reclamation of surface mines using non-waste materials is known and has been utilized on a commercial scale.

Costs:

Are site specific and depend on the quantity and type of waste handled, and on the number and type of erosion control measures implemented. For example, costs associated with the establishment of vegetation include cost of surface preparation, topsoil, mulching, seed and seeding, fertilization, irrigation and maintenance. Costs for vegetating disposal sites for the commercial-scale oil shale operation proposed for the Colony development operation have been estimated at $0.50 per square meter ($2,000 per acre), including topsoil(11). Certain costs associated with disposal in underground mines, such as modifications to ventilation systems, would not be applicable to surface mines.

C. Conventional Landfilling

Method involves disposal of solid waste/sludges on land with provisions for minimizing environmental contamination. Landfill operations range from open dumping of debris to controlled disposal in "secure" or "sanitary" landfills. Open dumps, in which wastes are piled on the surface of the terrain, are prohibited in most states and are to be totally phased out under the provisions of the recently enacted Resource Conservation and Recovery Act (RCRA). In sanitary landfills, the wastes are usually compacted to confine them to the smallest practical area, and then are covered with a layer of soil at regular intervals (usually at the end of a day's operations)(3).

Applications: Landfills have been widely used for the disposal of municipal refuse and a range of industrial wastes. Landfilling is currently the most prevalent method of disposal of petroleum refinery solid wastes (e.g., solids and sludges from pollution control processes, spent catalyst, tars, fly ash, and miscellaneous plant refuse)(4). Although there are no known applications to each gasification facilities, landfilling would be suitable for the disposal of ash, other inorganic solids/sludges, chars, sludges from biological treatment, and possibly unrecyclable spent catalysts and related materials. Highly hazardous waste may be "chemically" fixed ("passified") or encapsulated prior to placement in landfills.

Development Status: Commercially available.

Methods of Operation: The principal methods used in landfilling are classified as: (a) area; (b) trench, and (c) depression. In the area method, wastes are spread on the surface of the land in long, narrow strips that vary in depth from 0.40 - 0.65 m (16-30 in). Each layer is compacted until the thickness of the compacted wastes reaches 1.8 - 3.1 m (6-10 ft). A 0.15 - 0.30 m (6-12 in) layer of soil is then placed over the waste. In this trench method, wastes are placed in trenches varying from 30.5 - 122 m (100-400 ft) in length, 0.9 - 1.8 m (3-5 ft) in depth, and 5 - 8 m (15-25 ft) in width. The waste is compacted and added until the desired height is reached, then is covered with soil. The depression method is similar to the trench method, except that natural or artifical depressions are used to contain the waste(1).

Design Factor: Factors that must be considered in designing and evaluating landfill sites include: (a) available land area; (b) soil conditions (which affect pH and sorptive capacity) and topography; (c) geologic conditions (rock type, geologic structure, and weathering characteristics); and (d) hydrology (permeability, depth to water table, direction and rate of groundwater flow; (e) climatological conditions; and (f) potential ultimate uses for the completed site. Provisions must be made in landfill design for diversion and control of surface waters, for leachate collection, for gas venting, for inclusion of impermeable liners, and for monitoring wells. Cover materials or liners may be required to suppress air emissions. Incompatible wastes may require segregation prior to compaction.

Economics: Investment costs are usually low. Operating costs depend upon the method of operation, the cost of labor and equipment (e.g., motorized machinery, tools, facilities, fences, drainage pipes, cover material, etc.), and the efficiency of the operation. Cost for various liners are shown in Table F-2.

TABLE F-2. LINER COSTS(6)

Liner Type	Cost per Acre (1978)
Clay	$ 1,185
Asphalt	$ 6,000 - $12,000
Rubber	$11,000 - $22,000
Hypalon	$11,000 - $22,000
Polyvinyl Chloride (PVC)	$ 4,840 - $ 9,680

Advantages(1,7)

- Usually the most economical method of solid waste disposal; initial investment is usually low compared to other methods.
- Suitable for many types of wastes, if adequate provisions for environmental protection are employed.
- Method is flexible; wide variations in waste loads are readily accommodated.
- Land may be reclaimed for use as parking lots, playgrounds, golf courses, etc.

Disadvantages(5,7)

- Leachate generated from the waste during compaction or filling activities, or due to rainwater/snowmelt seepage, may contaminate groundwater unless adequate leachate containment methods are employed.

- Suitable land may be unavailable within economic hauling distance of a coal gasification facility.
- Requires daily and periodic maintenance to prevent environmental contamination.
- Landfills located in or near residential areas can evoke public opposition.
- If improperly vented, landfills may generate explosive or hazardous concentrations of methane and other gases, which may interfere with the use of the landfill or create a nuisance.

D. Soil Application(8,9,10)

Disposal of solid waste by mixing into topsoil. Organic material in the waste undergoes degradation through microbial action, and inorganic components of the waste are slowly released into the soil, thereby increase in its nutrient content. Soil application may incorporate production of crops (e.g., alfalfa) which would offset commercial disposal costs.

Applicability: Method is applicable to the disposal of waste biosludge, oily sludges and ash. Alkaline ash is particularly useful in soils containing pyritic sulfur such as that near coal mines, which slowly decompose to acidic products.

Operating Conditions: Waste is distributed on the land in one of three ways: the "spreading" method, the "flooding" method, and the injection method. In the spreading method, waste is spread over the land directly from the tank trucks, or pumped or gravity fed through pipelines to the agriculatural land or land to be reclaimed. In the flooding method, a plot of land is flooded with the waste and allowed to remain idle until most of the water is evaporated. Once applied to the land and dried, rototillers or plows can be used to homogenize the waste into the soil to depths or up to 51 cm (20 in.).

Some design consideration and process variables involved are: waste composition, including toxics concentration, soil composition, nutrient content and moisture, proximity to surface waters and distance to groundwater table, nutritional value of the waste, land availability, transportation costs, effects on vegetation, and atmospheric and climatic conditions. The actual depth of application is determined by experience. The rate of degradation and disappearance of the waste depends upon the thickness of of the waste deposit, the frequency of tilling and the amount of fertilizer used.

Development Status: Soil application of digested sludges from small municipal wastewater treatment plants is common in the U.S. and Europe, particularly in arid and semi-arid regions. The method is also being used by a number of petroleum refineries. For example, in the Bakersfield, CA. area in drilling wastes, miscellaneous oily sludges and acid sludges from petroleum refineries are being applied to land at waste disposal "farms" (California Class II-1 disposal sites).(10)

Advantages:

- Nutrients present in the waste tend to improve soil texture, water retention, and overall ability to support vegetation.
- Minimal or no formation of undesirable odors or leachates.
- Minimal disturbance of the land.
- Method is flexible; wide variations in waste loadings are readily accommodated.

Disadvantages:

- Wastes containing high concentrations of toxic compounds or having an unfavorably high or low pH cannot be successfully treated.
- Method is dependent upon availability of land and proximity to waste generation site.
- Aerobic conditions are usually maintained only within the top 10 - 15 cm (4-6 in.) of the soil; hence, periodic plowing of the soil and rotation of the waste-receiving plots may be required to enhance oxygen transfer between the ambient atmosphere and the wastes. Waste accumulations and odor problems may occur under anaerobic conditions.
- Inadequate design of land application sites may result in run-off of material into receiving waters or contamination of groundwaters.

Cost: Depend on the soil application process utilized, on the quantity of waste handled, haulage distance to the disposal site, and costs of periodic plowing to enhance oxygen transfer capabilities of the soil. Costs also include disposal fees charged by private operators; at the Bakersfield waste disposal farms, general rates charged ranged from 0.10 to 3¢/liter (15¢ to 35¢/bbl).(10)

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CHEMICAL FIXATION AND ENCAPSULATION

1.0 General Information

1.1 Operating Principle - Chemical fixation (also known as cementation, waste passification or waste immobilization) employs fixation chemicals which are mixed with the waste for the purpose of solidifying the wastes prior to encapsulation and/or disposal. Encapsulation is a process in which the fixed or untreated wastes are containerized or coated with inert materials in preparation for ultimate disposal.

1.2 Development Status - Only a few processes are commercially available and have been used both domestically and abroad (e.g., primarily Europe and Japan); most processes are in early developmental stages.

1.3 Licensor/Developer - Several chemical fixation and encapsulation processes are available through commercial suppliers, such as Chemfix, Inc. (Pittsburgh, Pa.) and Crossford Pollution Services, Ltd. (Sole, England). A complete listing of available processes is available in the literature(1).

1.4 Commercial Applications - Chemical fixation and encapsulation processes have been applied to wastes from numerous industries, including chemical, petrochemical, and metal finishing industries(2). (Most applications to date have been abroad; however, usage is gaining interest in the U.S.) No known application to coal gasification wastes.

2.0 Process Information

2.1 Flow Diagram - See Figure F-2 for the Chemfix Process

- Process Description - The specific operations and equipment employed in chemical fixation vary from process to process and

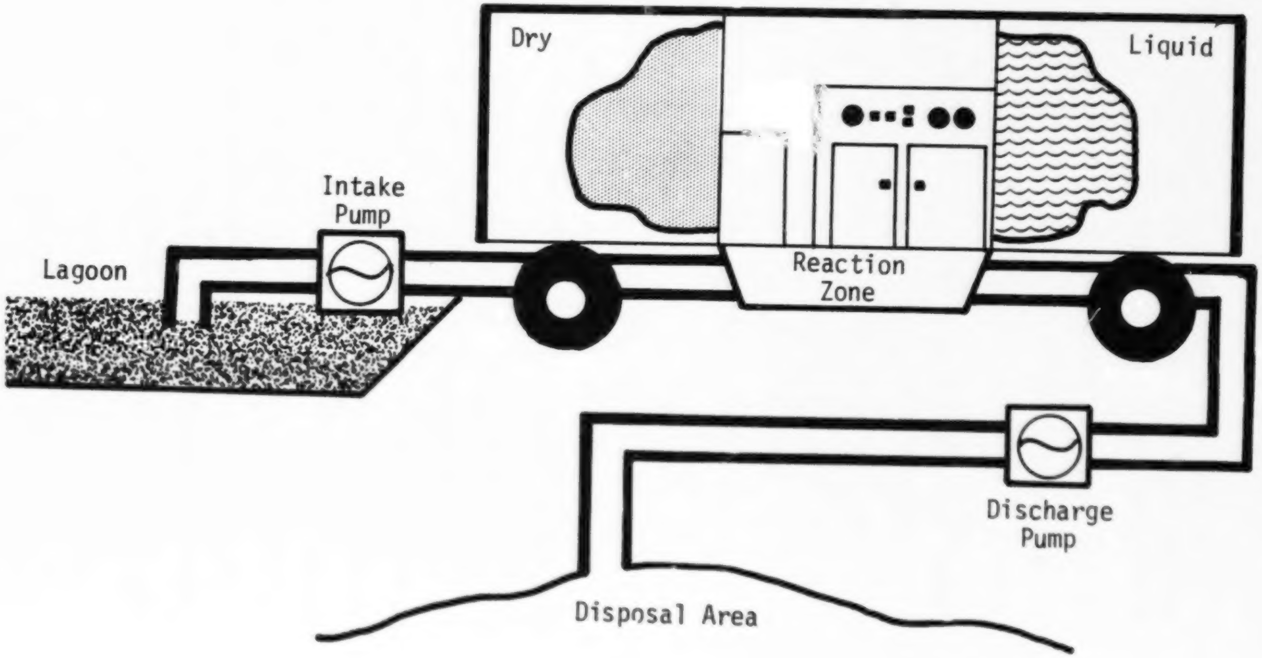
Dry
Liquid
Intake Pump
Lagoon
Reaction Zone
Discharge Pump
Disposal Area

Figure F-2. Schematic of Chem-Fix Process(2) in many cases are proprietary. In the schematic of the Chemfix Process shown in Figure F-2, the waste is pumped through a reaction tank located in a mobile van. Proper amount of the fixation chemical (a soluble silicate formulation containing setting agents) is mixed with the waste. After proper reaction time, the mixture is discharged to the final disposal area.

Plastic and metal drums and concrete, asphalt and resins have been used for containerization and encapsulation of untreated wastes or chemically fixed wastes.

2.2 Equipment - Vary with the process; equipment may include mixing chamber, pumps, metering devices, mechanical stirring devices, and chemical storage tanks.

2.3 Feed Stream Requirements(3) - Wastes may require stabilization prior to fixation/encapsulation for two purposes: 1) to make the waste more compatible with the solidification step, and 2) to convert the wastes into a chemical form that is more resistant to leaching in the ultimate disposal site. The most common stabilization process is pH adjustment; most cementitious fixation processes require a pH between 9 and 11.

2.4 Operating Parameters - Vary with the specific process used and waste being treated. Major parameters include waste: chemical ratio, retention and drying times, and temperature.

2.5 Process Efficiency and Reliability - The effectiveness of a fixation process depends upon the type of process used, and on the nature of the waste being treated. The most important criteria of effectiveness are mechanical strength and resistance to chemical attack (e.g., by leachate in a landfill environment) and biodegradation. Standard laboratory leaching tests have been devised to evaluate the effectiveness of fixation/encapsulation methods(2). Table F-3 presents typical leaching study results for some refinery wastes stabilized by the Chemfix process.

TABLE F-3. LABORATORY LEACHING RESULTS OF CHEM-FIXED REFINERY WASTES(2)*

Constituent	Conc. in the Raw Sludge ppm	Cm. of Leachate Water†			
		0-62	62-125	125-188	188-250
Total Chromium (Cr)	43.5	<0.10	<0.10	<0.10	<0.10
Iron (Fe)	1310	<0.25	<0.10	<0.10	<0.10
Zinc (Zn)	88.0	<0.25	<0.10	<0.10	<0.10
Nickel (Ni)	8.9	<0.25	<0.10	<0.10	<0.10
Copper (Cu)	0.62	<0.25	<0.10	<0.10	<0.10
Manganese (Mn)	-	<0.25	<0.10	<0.10	<0.10
Cyanide (Cn)	-	<0.10	<0.10	<0.10	<0.10

*Concentration of the constituents in ppm in the leachate water after application of the specified amount of distilled water.

†Each 62 cm (25 in.) of leachate water represents approximatly 80 ml of distilled water.

2.6 Raw Materials Requirements

- For chemical fixation: Portland cements; pozzolanic cements; lime-based mortars; asphalt; polybutadiene; silicate; ion-exchange resins; epoxies, and various proprietary formulations (e.g., Chemfix Process).
- For encapsulation: concrete, metal or steel containers, or self-setting resins.
- pH adjustment chemicals (e.g., sulfuric acid, sodium hydroxide, etc.).

2.7 Utility Requirements

Electricity: For driving pumps, mechanical stirring apparatus, and other equipment as required. Requirements dependent upon the specific process used and volume of waste handled.

3.0 Process Advantages(2,3)

- Highly hazardous wastes can be disposed of in a landfill after chemical fixation/encapsulation.
- Chemicals in the solidified/encapsulated wastes are not accessible to biodegradation or leaching; minimizes leachate formation from landfills.
- In some processes, wastes with high water content can be processed without water discharge from the process.
- Some process applicable over wide ranges of waste composition.

4.0 Process Disadvantages(2,3)

- Relatively high cost.
- Applications generally limited to small volume, high toxicity wastes.
- Durability and long-term performance of most processes under influence of environmental conditions (e.g., weather, microorganisms, light) are not known.

5.0 Process Economics(5,6)

Costs of chemical fixation and encapsulation processes are generally high. An engineering estimate for the chemical fixation of flue gas desulfurization sludge (including final disposal) is $8 to $13/tonne ($7.2 to $11.8/ton).

6.0 Input Streams

- Influent waste - may include heavy metals, and complex mixtures of organic and inorganic materials.
- Chemical fixation materials - see Section 2.6.

7.0 Discharge Streams

- Solidified, encapsulated waste.

8.0 Data Gaps and Limitations

Essentially nothing is known about the applicability of fixation/ encapsulation of wastes from coal gasification.

9.0 Related Programs

None known.

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